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Contents

Phosphoramidite-Controlled Asymmetric Hydrogenation with Rhodium Catalysts 54
By David J. Ager, André H. M. de Vries and J. G. de Vries

6th International Workshop on Catalytic Combustion 64
Reviewed by Reza Torbati

Precious Metal Finishing Revisited 67
Reviewed by Alan Boardman

Thermophysical Properties of Rh₃X for Ultra-High Temperature Applications 69
By Yoshihiro Terada, Kenji Ohkubo, Seiji Miura and Tetsuo Mohri

Plaque to Osmium and Iridium Discoveries 77
By W. P. Griffith

Platinotype Sets Record Price for Photographs 78
By Mike Ware

Ruthenium Allenylidene Complexes 81
By Ileana Dragutan and Valerian Dragutan

Role of Ruthenium in Organic Chemistry 95
Reviewed by Laura Ashfield

The Discoverers of the Palladium Isotopes 97
By J. W. Arblaster

Nitrous Oxide Greenhouse Gas Abatement Catalyst 103
By T. Kopperud

Abstracts 104

New Patents 108

Final Analysis: Sulfur as a Catalyst Poison 110
By J. K. Dunleavy

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Phosphoramidite-Controlled Asymmetric Hydrogenation with Rhodium Catalysts

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Phosphoramidites, and in particular those derived from BINOL, the MonoPhos family of ligands, have proven extremely useful for the asymmetric hydrogenation of carbon–carbon unsaturation using a rhodium catalyst. Many classes of alkenes can be reduced by these catalyst systems. The use of high-throughput experimentation can be applied to the synthesis of MonoPhos ligands and their subsequent screening, in order to find an appropriate candidate for a specific transformation. Suitable mixtures of ligands can also be found by these high-throughput methods.

The finding by Knowles, building on the observation of Kagan (1, 2) with diop, 1, that a bisphosphine ligand led to high asymmetric induction when compared with a monophosphine, gave rise to the development of the dipamp, 2, ligand for the asymmetric hydrogenation of enamides (3, 4). Since that time, an abundance of bisphosphines have been developed to perform asymmetric reductions of a wide variety of substrates (5, 6). The reason behind this move to bidentate ligands is the argument that there is increased rigidity in the metal–ligand complex (6). However, until relatively recently, little attention had been paid to monodentate ligands, such as phosphoramidites, as agents to perform asymmetric hydrogenations.

It had already been established that phosphoramidite ligands could effect high enantioselectivities for conjugate additions of alkylzinc agents to enones (7). The precedent for asymmetric reactions with this class of ligand had thus been established. In addition, since phosphoramidites can be considered modular, as the diol and amine moieties can be varied a large library of these ligands is readily available. Some of this work on phosphoramidites in asymmetric hydrogenations has already been reviewed (8–14).

1. Reductions to α-Amino Acid and α-Alkyl Succinic Acid Derivatives

The first phosphoramidite to be investigated for asymmetric hydrogenations was MonoPhos™, 3a. It was satisfying to find that the asymmetric hydrogenation of an enamide resulted in significant enantioselectivity. The degree of asymmetric

\[ \begin{align*}
\text{R}^1 = \text{R}^2 &= \text{Me} \quad \text{(MonoPhos)} \\
\text{R}^1 = \text{R}^2 &= \text{Et} \\
\text{R}^1 = \text{R}^2 &= -(\text{CH}_2)_5- \quad \text{(PipPhos)} \\
\text{R}^1, \text{R}^2 &= -[(\text{CH}_2)_2]_2 \text{O} \quad \text{(MorfPhos)} \\
\text{R}^1 = \text{H}, \text{R}^2 &= (\text{R})-\text{CHMePh} \\
\text{R}^1 = \text{H}, \text{R}^2 &= \text{i-Pr}
\end{align*} \]
induction was found to be solvent dependent, with dichloromethane and ethyl acetate, in general, providing the highest selectivities. \( \alpha \)-Amino esters \((R^1 \neq H)\) and acids \((R^1 = H)\) as well as \( \alpha \)-substituted succinate esters were produced in high enantiomeric excesses (ees) (Schemes I and II) (15, 16).

A simple variation in the substituent on the nitrogen to the diethyl analogue, 3b, of MonoPhos led to higher ees for the reductions of \( \alpha \)-(acylamino)acrylates to \( \alpha \)-amino ester derivatives (17). This enhancement was improved by the use of PipPhos, 3c, and MorfPhos, 3d, for the preparation of \( \alpha \)-amino acids and succinates (18).

It was found that bidentate ligand 4 gave lower ees in the reduction of enamide esters \((\text{cf. Scheme I})\) than the monodentate ligand 3a (15). However, others found that the use of a different diamine bridge, as in 5, could provide an ee up to 90\% for an itaconic ester reduction \((\text{cf. Scheme II})\) (19).

Just prior to the first publication describing hydrogenation by MonoPhos, it had been noted that the bidentate ligand QUINAPHOS, 6, which possesses a phosphine group as well as a phosphoramidite, could provide high ees for the hydrogenations shown in Schemes I and II (20).

The diol backbone does not have to be derived from BINOL (bis-\( \beta \)-naphthol) to achieve high asymmetric induction for the hydrogenations of enamides to \( \alpha \)-amino acid derivatives, and of itaconic acid and esters to succinates. The spirocyclopentane derivatives, SIPHOS, 7, provide one family of successful ligands (21), although the phosphoramidites, 8, derived from D-mannitol did not give high ees for these reductions (22).

The H\textsubscript{8}-BINOL derivative, 9a, also showed increased enantioselectivities compared with

\begin{align*}
\text{Scheme I} \\
\begin{array}{c}
\text{enamide} \\
\text{Rh(COD)\textsubscript{2}BF\textsubscript{4}, 3a (2.2 eq.)} \\
\text{CH\textsubscript{2}Cl\textsubscript{2} or EtOAc, H\textsubscript{2}} \\
\text{\( \alpha \)-amino esters and acids}
\end{array}
\end{align*}

\begin{align*}
\text{Scheme II} \\
\begin{array}{c}
\text{itaconic ester} \\
\text{Rh(COD)\textsubscript{2}BF\textsubscript{4}, 3a (2.2 eq.)} \\
\text{CH\textsubscript{2}Cl\textsubscript{2} or EtOAc, H\textsubscript{2}} \\
\text{\( \alpha \)-substituted succinate esters}
\end{array}
\end{align*}
MonoPhos, 3a, for the reductions of α-dehydroamino acids (23).

Another class of phosphoramidites that has proved successful for the synthesis of α-amino esters is DpenPhos, 10, (24). The highest ees were seen for bulky substituents on the imide nitrogens ($R_1 = 3,5-\text{-t-Bu})_2\text{C}_6\text{H}_3\text{CH}_2$), although the simple benzyl ($R_1 = \text{PhCH}_2$) does give acceptable values. The change from a methyl group in 10 ($R = \text{Me}$) in the phosphoramidite itself to the bulkier ethyl ($R = \text{Et}$) was detrimental to asymmetric induction. These ligands, 10, also provided good enantioselectivity for the hydrogenation of dimethyl itaconate (24).

Another variation on the atropisomeric theme which provides high asymmetric induction for the preparation of α-amino acid and succinic acid derivatives is the spirocyclic system, 11 (25).

With BINOL as the backbone of the phosphoramidite, variations are available for its modification. The simplest substitutions to perform are the symmetrical ones at the 3,3'- and 6,6'-positions, 12a and 12b, respectively (16). As will be seen, these substitutions can be important to achieve high degrees of asymmetric induction. The substituted BINOLs are simply used in place of BINOL in the phosphoramidite syntheses (see Section 6).

A system with only a 3-substituent on the BINOL moiety has been prepared, 12c. The asymmetry in the system also makes the phosphorus a stereogenic centre. Reductions of dehydroamino acids and itaconates proceed with high selectivities in most cases. The chirality of the BINOL moiety controls the stereochemical outcome of the reaction (26).

The coupling of a BINOL with a ferrocene-based system, as in 13a, leads to high turnover numbers while still retaining high enantioselectivities for the reductions of an α-amidoacrylate ester and itaconate (27, 28). Although two stereogenic moieties are present in the ligand, the stereochemistry of the BINOL controls the stereochemical outcome of the reaction even though there is a phosphine group on the ferrocene unit. However, in the case of mismatched chirality in the subunits, the enantioselectivity can suffer (29).

The use of an octahydrobinaphthyl system has some advantages for reducing enamides (see
Section 2). This reduced system has also been used to modify the hybrid system, 14, to enhance the enantioselectivities for the preparation of α-amino esters and dimethyl succinates (30).

A phosphoramidite derived from the achiral catechol, 15, provides high ee for the synthesis of methyl α-amino esters. In this series the substitution pattern on nitrogen is extremely important, as N-alkyl-N-phenylethyl analogues give low ees (31).

An atropisomeric phosphoramidite can be incorporated into a polymer, but the ees for the α-amino acids and succinate produced are usually lower (32). A similar effect was seen when the catalyst was immobilised on an aluminosilicate (33). The use of the dendritic phosphoramidite ligands, 16a, showed that the dendrimer inhibited the formation of inactive rhodium–ligand species, as the ligand:metal ratio could be increased over the monomeric series. Reductions of methyl 2-acetamidocinnamate with the parent ligand, 16b, as well as with the dendrimers, 16a, gave enantioselectivities comparable to those obtained with MonoPhos, 3a, itself (34).

2. Reduction of Enamides

In addition to being used for the preparation of α-amino acid derivatives, enamides can be reduced to form amides using MonoPhos, 3a, as the chiral ligand (Scheme III). When the potential for E- and Z-isomers occurs in the substrate, 17, then the Z-isomer is reduced with high ee with MonoPhos, 3a, while the E-isomer gives substantially lower selectivity. Again, for this reaction, the ee has some solvent dependence (16, 35). It was found that in dichloromethane the E-isomer of the enamide (17, R = Et) underwent isomerisation to the Z-isomer; this isomerisation did not occur in ethyl acetate (16, 36). Higher ees were obtained for these reductions when the diethyl derivative of MonoPhos, 3b, was employed (17). Again, as in the reductions of dehydroamino acid derivatives,
the use of PipPhos, 3c, and MorfPhos, 3d, gave exceptional enantioselectivities for enamide reductions (18).

A solvent effect on enantioselectivity was also seen when the phosphoramidite (SIPHOS), 7, was used as the ligand, although very high ees could still be achieved for the transformation summarised in Scheme III. It was found that small groups on nitrogen gave the highest selectivity (21). The introduction of substituents at the 4- and 4'-positions of SIPHOS did not increase enantioselectivity compared to the parent system (37). The ees for enamide reductions can be improved by use of the H$_8$-BINOL analogue of MonoPhos, 9a (38). Even better improvements were observed with the catechol-derived phosphoramidite, 15 (31).

The use of the DpenPhos ligands, 10, also provides high enantioselectivities for the reduction of aryl enamides (24), while the hybrid ligand, 13a, also gives high turnovers (27, 28). In contrast, the reduced naphthyl analogue, 14, gives reduced enantioselectivities (30).

3. Reductions to β-Amino Acid Derivatives

By comparison with α-amino acid derivatives, β-amino acid derivatives have not been so easy to access by asymmetric hydrogenation. One of the problems is that the substrate (enamide) is usually formed as a mixture of the E- and Z-isomers. To some extent this has now been solved, and the E-isomer (the one easier to reduce as there is no internal hydrogen bond in the substrate) can now be prepared in good yield (without resorting to chromatography) (39). The reduction of the Z-isomer of the enamide with bisphosphines has not been easy to achieve. However, the MonoPhos derivative, 3e, was found to give good ees for the reduction of both the E- and Z-substrates (Schemes IV and V, respectively) (40). Although ligand 3e has a stereogenic centre in the amine moiety, the asymmetric sense of the reduction is controlled by the atropisomerism of the ligand.

Once a screening tool for ligand libraries had been developed (see Section 8 on screening) it became clear from the validation studies that the phosphoramidite ligand, 3f, derived from BINOL and isopropylamine gave the same enantioselectivities as 3e, but the reduction was about five times faster (41).

Unlike other reductions with phosphoramidites, the best ligands to produce a β-amino acid derivative contain a proton on the nitrogen atom. This has been shown to be crucial to high selectivity with other systems, for instance, using hybrid ligand, 13b (42).

4. Reduction of Enol Acetates and Carbamates

Enol acetates and carbamates can be reduced in the presence of phosphoramidite ligands (Scheme VI). The ligand PipPhos, 3c, and its octahydro analogue, 9b, have proved to be the most effective for this reduction (43). In addition, the highest asymmetric induction was observed with the N, N-diethyl carbamates (18, R$^1$ = Et). The overall transformation can be considered as the reduction of a ketone to a chiral secondary alcohol.

\[
\begin{align*}
\text{NHA}c & \quad \text{R}^1 \text{CO}_2\text{R}^2 \\
\text{Z-enamide} & \quad \text{Rh(COD)BF}_4, 3e, \text{i-PrOH} \\
\text{NHA}c & \quad \text{R}^1 \text{CO}_2\text{R}^2 \\
\beta\text{-amino acid derivative} & \quad \text{ee 92–95%} \\
\end{align*}
\]

\[
\begin{align*}
\text{NHA}c & \quad \text{R}^1 \text{CO}_2\text{R}^2 \\
\text{E-enamide} & \quad \text{Rh(COD)BF}_4, 3e, \text{CH}_2\text{Cl}_2 \\
\text{NHA}c & \quad \text{R}^1 \text{CO}_2\text{R}^2 \\
\text{ee 98–99%} & \\
\end{align*}
\]
5. Reduction of \( \alpha,\beta \)-Unsaturated Acids

Reductions of \( \alpha,\beta \)-unsaturated acids (Scheme VII) can be accomplished by MonoPhos ligands. However, it seems that the substitution in the BINOL system helps with enantioselectivity, as illustrated by the 3,3'-dimethyl derivative, 12d (44). Also, the presence of an additional phosphine ligand, as discussed in Section 8, can enhance the enantioselectivity significantly, even when the phosphine is achiral.

6. Phosphoramidite Variations and Synthesis

Although phosphoramidites can provide useful monodentate ligands to effect asymmetric hydrogenations over a wide range of carbon–carbon unsaturation, some variation in structure is required to obtain high enantioselectivity and reactivity. This is also an issue with other classes of ligands, when even a minor variation in a bisphosphine structure can result in a lengthy synthesis having to be undertaken to achieve the desired end product. By contrast, the MonoPhos family is simple to modify, and the reaction parameters can be modified by the use of other ligands (Section 8).

As with bisphosphines, empirical means have to be used to find the optimal balance between reaction rates, catalysis usage and stereoselectivity. (This article focuses on rhodium, but other metals may be used.) Some general rules can be drawn:

- using a 3,3’-disubstituted BINOL as the backbone results in slower reactions (16);
- protic solvents (with the exception of isopropanol) are less suitable (15, 16);
- lower temperatures increase enantioselectivity (15, 16); and
- an increase in hydrogen pressure increases the reaction rate without affecting enantioselectivity (13, 15, 16).

However, the subtle differences in reactivities between different groups on the nitrogen are not simple to predict (13), and screening studies are the best way to establish the best ligand for a reaction. Indeed, the ease of synthesis of the MonoPhos family of ligands lends itself to application in rapid screening methodology.

MonoPhos, 3a, is simple to prepare in high yield from BINOL (bis-\( \beta \)-naphthol) and hexamethylphosphoruss triamide (HMPT) (45). In addition to the parent, 3a, the structure of the BINOL-derived phosphoramidites is simple to vary, merely by the use of a different amine in a modified synthetic sequence (Scheme VIII) (17, 46–48). A lithium amide can also be used in place of the reactive amine and base (16, 46). The amine group can also be modified by an amine exchange.
reaction with MonoPhos, 3a, in the presence of tetrazole (Scheme IX) (16, 40, 48). For bulky amines, the reverse sequence to Scheme VIII has proven advantageous (Scheme X) (16, 23, 49).

7. Mechanistic Considerations

Although just over two equivalents of the MonoPhos ligand, compared to the rhodium metal precursor, were used in the initial studies, a systematic series of experiments showed that reducing the amount of the phosphoramidite ligand to 1.5 equivalents, and even less, led to slightly faster reaction rates without any deleterious effect on the asymmetric selectivity (16, 48). Enantioselectivity does not alter during the course of a hydrogenation. When a number of reactions are compared a slight positive asymmetric amplification is seen (16). The mechanism of the reaction is far from being understood. However, it does seem that two phosphoramidite ligands are needed on the rhodium to explain the asymmetric amplification. Presumably, the two ligands generate the chiral environment, although it is not known how many phosphoramidites are on the metal in the key reduction step, as one phosphoramidite could have been displaced.

The use of slightly under two equivalents of the ligand can be explained by the many equilibria that are taking place in the reaction media and the formation of rhodium species (with three or four phosphoramidite ligands). These seem to be thermodynamically favoured structures which do not take part in the asymmetric hydrogenation (16).

Studies with the SIPHOS system, 7, showed that reductions of dehydroamino esters were of zero order in the concentration of the substrate, and first order in hydrogen pressure. The reaction was also first order with respect to the rhodium catalyst, but the rate of hydrogenation decreased as the metal:ligand ratio was increased (50). These findings parallel the results obtained with the MonoPhos system (51).

In addition to variations in the ligand structure itself, increased asymmetric induction and reaction rates can also be seen when a second ligand, either chiral or achiral, is added. As an example, for the reactions...
formation of β-amino esters (cf. Scheme IV), the use of one equivalent of ligand 3e with one equivalent of the octahydroBINOL-derived ligand, 9a, resulted in higher ees and reaction rates than for either ligand by itself (52). A similar result had been observed by Reetz with phosphites and phosphonites in other reductions (53).

This use of mixtures greatly increases the number of possible permutations with chiral ligands: just ten examples give rise to fifty-five different combinations. Obviously, this mixing is not available with bisphosphine ligands.

Phosphoramidite monodentate ligands can also be used in combination with phosphite ligands, which may also be chiral. When a tropos backbone based on the biphenyl system, 19, was used with two different chiral amine moieties for the formation of N-acetyl alanine, only moderate enantioselectivities were observed; these were generally lower than when a single phosphoramidite was used. However, reaction rate and asymmetric induction could be increased by a mixture of a phosphite, 19c, and the phosphoramidite, 19a or 19b. The initial screening gave a combination of ligands that achieved an 87% ee for the reduction. Optimisation of the reaction parameters increased the selectivity to 94% ee (54).

Thus, mixtures of ligands can potentially improve performance in reductions of α- and β-amino esters, enamides, and itaconates, as compared with the use of a single chiral ligand. For instance, a mixture of 19d and 19e performed the best in preparing α-amino acids, as outlined in Scheme I (55).

In general, asymmetric hydrogenations with monodentate phosphoramidite are slower than comparable ones with a phosphite ligand (55). A comparative rate study showed that monodentate ligands can perform at comparable rates on a specific substrate when the monodentate ligand is a phosphite or a phosphoramidite with one of groups on the nitrogen being a proton, as in 3e (56). MonoPhos, 3a, is significantly slower in asymmetric reductions than phosphite or bisphosphine ligands.

When a mixture of ligands is employed, the stoichiometry of the mixture may affect reaction rate. The use of a phosphite with a phosphoramidite results in a faster reduction than when just a phosphoramidite is employed. For optimal enantioselectivities, non-stoichiometric mixtures often give the best results (55).

8. Screening

The ease of synthesis of these ligands, and the need to investigate the reaction parameters to ensure high reaction rates and selectivities, are highly suited for high-throughput screening reactions (48).

A protocol has been designed for the parallel synthesis of ligand libraries in 96 well plates. A discrete ligand is prepared in each individual well. Key to the process is the removal of the chloride ions, as these can be detrimental to the asymmetric hydrogenation (21, 57). Filtration was found to be the easiest and best procedure for the removal. The resultant solution can then be evaporated in order to change the solvent from toluene (used in the ligand preparation step) to the reaction solvent. Substrate and metal precursor are then added, using a robot, and parallel hydrogenation reactions can then be performed. This method was
validated for the reductions of methyl N-acetyl-
aminocinnamate and methyl 3-(N-acetoamido)but-2-enoate. The trends were the same as those seen with purified ligands, although the ees were slightly lower (41).

The high-throughput method can also be used to screen mixtures of ligands, and this includes examples with the addition of achiral phosphines. For the reductions of α,β-unsaturated acids (58, 59), the addition of an achiral phosphine was found to enhance the reaction rate and enantioselectivity (Scheme XI) (44).

The rate of a reaction can be monitored via hydrogen uptake. An Endeavor® catalyst screening system is used in our laboratories, and this can monitor eight independent reactions at the same time (16). The ligand library approach can also be used for reactions other than asymmetric hydrogenations, as has been illustrated with conjugate additions to cyclic enones (58, 59).

Conclusions

Phosphoramidites, and in particular those derived from BINOL, the MonoPhos family of ligands, have proven extremely useful for the asymmetric hydrogenation of carbon–carbon unsaturation using a rhodium catalyst. The simple sequence to prepare these MonoPhos ligands, combined with the cheap starting material, makes them very competitive at an industrial scale when compared with bisphosphine ligands. Another advantage of the simple synthetic sequence is that it has been adapted for high-throughput experimentation, which allows for rapid screening for an appropriate ligand. The high-throughput experimentation can also be used to define reaction parameters.

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André H. M. de Vries has a Ph.D. (University of Groningen) on asymmetric catalysis. During his Ph.D. he introduced monodentate chiral phosphoramidites (including MonoPhos) as highly successful ligands for conjugate addition reactions of dialkylzinc reagents to α,β-unsaturated ketones. He was a post-doctoral worker at Oxford University (Prof. John M. Brown) on asymmetric hydrogenations. He joined DSM in 1998, and currently is R&D Coordinator Chemistry and Homogeneous Catalysis. He is interested in homogeneous catalysed transformations; in particular, clean C-C bond formations and asymmetric catalysis, especially for the fine chemicals industry.

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The 6th International Workshop on Catalytic Combustion (IWCC6), organised by the Italian Chemical Society, took place on the wonderful Isle of Ischia, Italy, from 11th to 14th September 2005. The workshop provided a forum in which research and development managers, combustion engineers and catalysis scientists could share the latest information on developments and business opportunities in catalytic combustion. The technical sessions of the workshop used a variety of formats: keynote lectures, oral presentations and poster exhibitions. In total more than 110 contributions from industrial and academic scientists from about 30 countries were presented. In this review some of the highlights reported on catalytic combustion using the platinum group metals (pgms) will be described.

Catalytic combustion is now established as a benchmark technique for the abatement of volatile organic compound (VOC) emissions, but it is still at an early stage of evolution as a commercial technology for producing heat and energy. The development of catalytic combustors operating under fuel-rich conditions has provided a new impulse towards commercialisation. Such combustors may generate hydrogen-enriched streams, capable of stabilising homogeneous reactions and minimising emissions when integrated with gas turbine installations. Other areas showing great potential for fuel-rich catalytic combustion include fuel cells, and aftertreatment and cold start-up technologies for automotive applications.

Several workshop contributions concerned catalytic combustion for the abatement of VOC emissions, with particular focus on reducing emission of methane (CH₄) from compressed natural gas (CNG) engines, and high-temperature or ultra-lean applications.

Catalytic Combustion of Methane

In the course of a keynote lecture, Luca Basini (EniTecnologie SpA, Italy) briefly reviewed the fundamentals of the short contact time (SCT) phenomenon, in which hydrocarbon oxidation is induced by collisions lasting a few milliseconds between premixed gaseous reactants flowing over extremely hot catalytic surfaces. These conditions determine a rapid and selective reaction path, confined inside a thin (< 1 µm) solid/gas interphase zone surrounding the catalyst particles. Here the molecules spend 10⁻⁶ seconds at temperatures which may vary between 700 and 1300°C. These conditions favour the formation of primary reaction products, and inhibit chain reactions and product degradation. Basini discussed the application of SCT in developing technologies for hydrogen and synthesis gas production for refinery operations, and gas-to-liquid (GTL) transformations.

Rhodium/perovskite (Rh/LaMnO₃) structured catalysts were shown by S. Cimino and colleagues (Istituto di Ricerche sulla Combustione (CNR), Napoli, Italy) to be active in CH₄ combustion under fuel-rich conditions; this results in high CH₄ conversion and selectivity to H₂ and CO. The addition of perovskite enhanced activity by stabilising Rh at higher operating temperatures, at the same time promoting complete oxidation and inhibiting coke formation.

V. A. Sadykov and coworkers (Boreskov Institute of Catalysis, Russia) discussed the role of platinum dispersion and oxygen mobility on Pt/ceria-zirconia oxide catalysts doped with La, Sm or Gd, for the selective oxidation of CH₄ to synthesis gas at short contact times. The authors demonstrated a correlation between the specific DOI: 10.1595/147106706X110574
rate of CH\textsubscript{4} transformation into synthesis gas at short contact times with lattice oxygen mobility and Pt dispersion. They suggested that small Pt particles were important for CH\textsubscript{4} dissociation, while efficient oxygen transfer from the support to the Pt sites prevented their coking. When the lattice oxygen mobility is high, as for Gd-doped samples, the rate of CH\textsubscript{4} transformation also reaches a maximum. However this is not reflected in a maximum for hydrogen formation due to a decline of synthesis gas selectivity. Too high an oxygen mobility results in combustion of activated C-H fragments and CO/H\textsubscript{2} products.

In order to clarify some aspects of the mechanism of CH\textsubscript{4} oxidation on palladium/\textgamma-Al\textsubscript{2}O\textsubscript{3} catalysts, O. Demoulin (Université Catholique Louvain, Belgium) et al. studied the behaviour of a 2 wt.% Pd/\textgamma-Al\textsubscript{2}O\textsubscript{3} catalyst, following oxidising or reducing pretreatment, using Raman and diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS). It was shown that under both a pure oxygen atmosphere and lean working conditions, the Pd is always in an oxidised form. Fully reduced Pd is not active at all for the catalytic combustion of CH\textsubscript{4}. The authors proposed that a layer of a very reactive oxygen species could develop on the surface of the Pd particles in these conditions. This would ensure optimal catalytic activity for CH\textsubscript{4} oxidation.

The use of aluminium borate as an effective new support for Pd catalysis in CH\textsubscript{4} catalytic combustion at high temperatures was investigated by R. A. Ghaleb and colleagues (Université Claude Bernard, Lyon, France). The catalytic behaviour of this novel system (2 wt.% Pd/Al\textsubscript{18}B\textsubscript{4}O\textsubscript{33}) was compared with that of 2 wt.% Pd/Al\textsubscript{2}O\textsubscript{3} catalyst. Both the fresh and aged Pd/Al\textsubscript{18}B\textsubscript{4}O\textsubscript{33} catalysts were more active in CH\textsubscript{4} combustion, with better activity – particularly after ageing at 800°C for 6 hours (O\textsubscript{2}, 10% H\textsubscript{2}O) – than 2 wt.% Pd/Al\textsubscript{2}O\textsubscript{3}. The higher activity in the Al\textsubscript{18}B\textsubscript{4}O\textsubscript{33}-supported catalyst was attributed to the stabilisation of PdO by strong interaction with Al\textsubscript{18}B\textsubscript{4}O\textsubscript{33}; this retarded the decomposition of PdO into Pd metal.

P. Gelin (Université Claude Bernard, Lyon, France) et al. presented interesting work on the catalytic properties of Al\textsubscript{2}O\textsubscript{3}-supported bimetallic Pt-Pd catalysts in the combustion of CH\textsubscript{4} under lean conditions at low temperatures. Catalytic activity was measured both in the presence and absence of 10% water vapour. The influence of steam ageing (10% H\textsubscript{2}O, 600°C for 22 hours) on the properties of the catalyst was also addressed. The addition of small amounts of Pt to the Pd (up to a Pd:Pt molar ratio of 4:1, with a constant 2 wt.% metal loading) was shown to produce more activity than the reference Pd/Al\textsubscript{2}O\textsubscript{3} catalyst, in spite of the decreasing Pd loading. The effect was even more pronounced after ageing. A thorough Fourier transform infrared (FTIR) spectroscopic study of CO adsorption on reduced catalysts (fresh or aged) revealed the existence of new surface sites having properties different from those of monometallic particles. This suggests the existence of bimetallic particles. On the basis of these results, together with those of dispersion measurements, the authors proposed that these new surface sites were responsible for the enhanced catalytic activity.

**Catalytic Oxidation in Automotive Exhaust Emission Control**

Martyn V. Twigg (Johnson Matthey Environmental Catalysts and Technologies, Royston, Herts, U.K.) gave a keynote lecture on the role of catalytic oxidation in the control of vehicle exhaust emissions. The session began with a brief history of catalytic oxidation and moved on to discuss the role that the precious metals, principally Pt, Pd and Rh, have played in improving oxidative reactions for both gasoline- and diesel-fuelled automotive applications. The importance of maintaining reactivity toward hydrocarbon and carbon monoxide, while limiting the formation of undesirable sulfur and nitrogen oxides, was emphasised. The more recent development of catalysed filter systems to remove particulates from diesel exhausts is an example of a novel oxidative use of NO\textsubscript{2} – as the oxidant for the trapped carbon-based particles.

In order to validate experimentally some proposed CO and H\textsubscript{2} oxidation reaction mechanisms
currently used for modelling platinum diesel oxidation catalysts, S. Salomons and coworkers (University of Alberta, Edmonton, Canada) studied the oxidation of CO and H₂, separately and then in combination. CO inhibits the oxidation of H₂, while H₂ promotes the ignition of CO. A Langmuir-Hinshelwood model gave a good prediction of CO light-off, but not of CO extinction (light-out). The presence of water was shown to delay CO ignition, but shifted the extinction to lower temperature.

**Posters on Methane Combustion**

The catalytic combustion of CH₄ and aromatic VOCs were emphasised in the large number of posters on display. A poster by L. M. Simplicio (Politecnico di Milano, Italy) described an investigation of the effect of PdO dispersion on the catalytic properties of PdO/Al₂O₃ catalysts towards CH₄ oxidation. After trying different Pd precursors and preparation routes, it was suggested that there was a relationship between PdO particle size and CH₄ conversion. Highly active catalysts had the smallest PdO particle size and the highest PdO dispersion.

In a separate study, the catalytic oxidation of CH₄ on alumina-supported Pd catalysts was investigated, as a function of temperature and time-on-stream, by O. Demoulin (Université Catholique Louvain). The activity of CH₄ combustion was found to increase with time-on-stream over the Pd/Al₂O₃ catalyst. This was related to the sintering of the Pd phase under reaction conditions; sintering was found to be beneficial for CH₄ combustion.

K. Persson (Royal Institute of Technology (KTH), Stockholm, Sweden) compared the catalytic combustion of CH₄ over Pd and Pd-Pt catalysts. The influence of the support material on bimetallic catalyst performance was also investigated. The study demonstrated that using bimetallic Pd-Pt (molar ratio 2:1) catalysts produced a much more stable CH₄ conversion than using a monometallic Pd catalyst. The support material influenced the catalytic activity of CH₄ combustion over Pd-Pt catalysts; for example, the Pd-Pt/Ce-ZrO₂ system reoxidises more easily than does the alumina-supported Pd-Pt catalyst.

**Conclusion**

The importance of pgm-based catalytic combustion as a way of producing heat and energy at much lower temperature, and thus with lowered emission of pollutants, such as CO and NOₓ, was highlighted throughout the workshop. The outstanding levels of performance obtained by catalytic combustion processes for emission control have provided the incentive for commercialisation of this technology, which is advancing towards a successful future.

A list of the oral and poster presentations given at this workshop is available on the website: http://www.iwcc6.unisa.it/

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**The Reviewer**

Dr Reza Torbati is a Senior Scientist in the Gas Phase Catalysis Group at the Johnson Matthey Technology Centre. His main interests are in the development of catalysts for diesel engine applications.
This is a revised, slightly updated and enlarged edition of the 2003 book by Terry Jones (reviewed in this Journal by A. S. Pratt (1)), with three new chapters added to the end. The cover title remains slightly misleading, since the book covers both electrodeposition and electroless deposition of the rare precious metals. Fused salt plating is also dealt with, along with two new chapters devoted to electropolishing and stripping of all precious metals. The emerging area of electroless platinum deposition is addressed in the last new chapter, and the scant references to the electroless plating of the rare precious metals are sensibly incorporated into the chapters on electrodeposition. Despite the inclusion of electroless platinum deposition, the development of electroless palladium plating for circuit boards, which is a commercial success, is not dealt with. Plating of precious metal/base metal alloys for data storage (for example, platinum-cobalt) is also absent.

As early as page two, the author justifies his inclusion of rhenium by comparing its scarcity and physical properties to those of other precious metals. The increasing popularity of induced electroless rhenium plating with nickel-phosphorus and other metals to form electronic barrier layers, as well as magnetics, may have been worth addressing in an extra page or two.

Nevertheless, this book, written in a simple and readable way, is a welcome introduction to rare precious metal plating. A typical chapter comprises a survey of the desirable properties and applications of the metal, a list of popular modern plating baths, their optimum working conditions, an extensive account of deposition properties and even analytical control. Nearly all baths referenced are post 1970, with only a few from the 1960s, so readers are not presented with the full historical development of many of the baths. Most references are from well known plating journals, for instance: *Journal of The Electrochemical Society, Metal Finishing, Plating and Surface Finishing, Transactions of the Institute of Metal Finishing* (the last one being the leading U.K. example) and other obtainable sources. Surprisingly, the author is a little short on applications for some metals, for instance rhenium and iridium, but this may reflect his greater knowledge of other metals dealt with in the book. Generally, the book places the metals in order of their industrial importance and plating success, beginning with popular rhodium. At fifty-seven pages, rhodium is allotted the longest chapter, half of it dealing with plating baths and half with deposition properties. The remaining metals have at least 20 pages devoted to each, except rarely used osmium stretched out at twelve pages.

Not surprisingly, the chapter on stripping metals is a little light, since precious metals are not noted for their ease of dissolution, from which the metal values must subsequently be recovered. However, recovery can be easily achieved using a precious metal scavenger, such as ion-exchange resin/fibre. This technology is not mentioned in the book. In general the book is well supported with equations, diagrams, graphs and tables.

**Practical Plating Baths**

Just how practical or useful some of the plating baths are depends on whether the reader has an academic or commercial interest – or has had the opportunity to evaluate them. From personal experience, the few plating baths I recognise in this book struggle to achieve the performance described. For example, it has always been difficult to find useful electroplating baths for pure iridium, and electroless iridium deposition remains in its
infancy. Electroless ruthenium plating baths are described; but stability, performance and deposition quality need further study and much improvement prior to commercial use. However, stable electroless platinum and platinum alloy plating baths can be constructed. They normally yield layers of 5–15 micron thickness, but greater than 30 micron thickness is achievable for demanding applications. After much research, Johnson Matthey marketed such baths ten years ago, under the TRIPLE-E® trade name, but with limited outside interest. Over the last decade, some in-house users have described working commercial electroless platinum plating baths, mainly for medical applications. This point is not highlighted in the book. Recently, an electroless platinum-rhodium alloy process has been patented by Honeywell Inc. (2). Electroless platinum is typical of areas of research where new applications have, for some years, stimulated industrial research but with restricted knowledge filtering into the open literature. As illustrated by these examples, the increasing speed with which new or improved precious metal deposition baths are reported will soon require the present book to be revised yet again.

This updated book may stimulate further research into new plating baths and into improving existing technology, and the author acknowledges his debt to two "bibles" of modern plating in his foreword (3, 4). The rise of electroless platinum and palladium plating should promote interest in the electroless plating of the other precious metals. However, safer compositions, a wider range of operating conditions, better bath stability and turnover still need to be achieved for many of the electroless compositions noted in this book. Indeed, the quality and durability of deposits are of concern, particularly for high-temperature, electronic and medical applications. While many of the technologies described here have been advanced by industry, this book serves as a good background to investigate this interesting area.

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The Reviewer

Alan Boardman has a Ph.D. from the University of Lancaster and researches into decorative metal coating at the Johnson Matthey Technology Centre. He conducted plating research for the Johnson Matthey Noble Metals Division from 1993 to 1998. His current interests include all metal plating and coating techniques, and the chemistry of the coinage and main group metals.
Nickel-based superalloys have been the principal high-temperature structural materials for gas turbine engines. Their properties have been improved significantly by alloying additions, directional solidification and by the use of single crystals (1). However, gas turbine engines have developed to the point where their operating temperatures are now close to the melting temperatures of these alloys. A new base material is therefore required if higher material temperatures are to be achieved.

Much contemporary research on high-temperature structural materials is centred on intermetallic compounds. Several reviews have addressed the potential for intermetallic alloys (2–7). Among intermetallics, rhodium-based L12 compounds offer advantages for high-temperature structural applications. First, the melting points are 300 to 700 K higher than those of nickel-based superalloys (8). Secondly, the L12 crystal structure offers the possibility of enhanced ductility and excellent workability as a result of the large number of possible slip systems. Finally, the two-phase γ/γ′-type microstructure formed in nickel-based superalloys can also be produced in rhodium-based alloys (9–11).

A preliminary study on the mechanical properties of the L12 intermetallic compounds Rh3X (X = Ti, Nb, Ta) is reported elsewhere (12). Rh3Ti shows good ductility up to 30% in compression, over a wide temperature range from room temperature to 1673 K, and both Rh3Nb and Rh3Ta show a positive temperature dependence of strength (a stress anomaly) at around 1273 K. However, by contrast with pioneering work on the mechanical properties of the rhodium-based L12 compounds, few studies on the physical properties of these compounds are found in the literature.

Thermal conductivity and thermal expansion were measured for the L12 intermetallic compounds Rh3X (X = Ti, Zr, Hf, V, Nb, Ta) in the temperature range 300–1100 K to evaluate the feasibility of applying the compounds as ultra-high temperature structural materials. The thermal conductivities of Rh3X are widely distributed over the range 32–103 W m⁻¹ K⁻¹ at 300 K, but the differences between the thermal conductivities diminish at higher temperatures. A trend is observed in that the thermal conductivity of Rh3X is greater if the constituent X belongs to Group 5 rather than to Group 4 in the Periodic Table. The coefficient of thermal expansion (CTE) values of Rh3X increase slightly with increasing temperature; values are concentrated around 10 × 10⁻⁶ K⁻¹ at 800 K. CTE values of Rh3X decrease as X appears lower in the Periodic Table. It is demonstrated that Rh3Nb and Rh3Ta are suitable for ultra-high temperature structural applications due to their higher thermal conductivities and smaller CTE values.
design parameters of structural materials. The rapid heat transfer afforded by high thermal conductivity enables efficient cooling which prevents the occurrence of life-limiting heat-attack spots. Higher operating temperatures can thus be sustained. Thermal expansion data are also required, with a view to minimising the thermal expansion mismatch in joints and thermal stress in components. Lower thermal expansion is desirable to avoid fatigue through thermal cycling, since thermal stress depends directly on the magnitude of the thermal expansion.

Rhodium-based compounds Rh₃X have L1₂ crystal structure, Table I, with constituent X belonging to Groups 4 and 5 in the Periodic Table (15). This study is designed to establish a basic data set for the thermal conductivity and the thermal expansion of the L1₂ intermetallic compounds Rh₃X (X = Ti, Zr, Hf, V, Nb, Ta).

### Thermal Conductivity

The thermal conductivities of Rh₃X at 300 K are summarised in Figure 1, where the thermal conductivity is plotted as the column height in the Periodic Table configuration. The largest thermal conductivity is found in Rh₃Nb and the smallest in Rh₃Ti. The following inequalities are observed:

\[
\lambda_{[\text{Rh}_3\text{Ti}]} < \lambda_{[\text{Rh}_3\text{V}]} \quad (i)
\]
\[
\lambda_{[\text{Rh}_3\text{Zr}]} < \lambda_{[\text{Rh}_3\text{Nb}]} \quad (ii)
\]
\[
\lambda_{[\text{Rh}_3\text{Hf}]} < \lambda_{[\text{Rh}_3\text{Ta}]} \quad (iii)
\]

where \(\lambda_{[\text{Rh}_3\text{X}]}\) represents the thermal conductivity of Rh₃X. \(\lambda_{[\text{Rh}_3\text{X}]}\) is therefore larger when X belongs to Group 5, rather than Group 4. The thermal conductivity of an intermetallic compound reaches a maximum at the stoichiometric composition, and decreases monotonically with increasing deviation from stoichiometry (16, 17). The hypothetical thermal conductivity of stoichiometric single-phase L1₂ Rh₃Hf is expected to be slightly greater than the experimental value for Rh-23.5 at.% Hf.

We have previously surveyed the thermal conductivities of B2 aluminides (FeAl, CoAl, NiAl), titanides (FeTi, CoTi, NiTi), and gallides (CoGa, NiGa) at ambient temperature (16). An empirical rule was found for compounds \(AB\), that thermal conductivity decreases monotonically with increasing horizontal distance, in the Periodic Table, of constituent \(A\) from constituent \(B\), that is:

\[
\lambda_{[\text{FeAl}]} < \lambda_{[\text{CoAl}]} < \lambda_{[\text{NiAl}]}
\]
\[
\lambda_{[\text{FeTi}]} > \lambda_{[\text{CoTi}]} > \lambda_{[\text{NiTi}]}
\]
\[
\lambda_{[\text{CoGa}]} < \lambda_{[\text{NiGa}]}
\]

The empirical thermal conductivity rule observed for B2 compounds is also observed in Rh₃X with the L1₂ crystal structure.

Figure 2 shows the thermal conductivities of Rh₃X as a function of temperature. A continuous decrease in thermal conductivity with increasing temperature is observed for Rh₃Nb, Rh₃Ta and Rh₃Zr, the thermal conductivities of which at 300 K are greater than 80 W m\(^{-1}\) K\(^{-1}\). By contrast, a considerable increase in thermal conductivity with increasing temperature is observed below 900 K.
for Rh₃Ti, which has a much smaller thermal conductivity at 300 K. The thermal conductivities of Rh₃Hf and Rh₃V are somewhat insensitive to temperature. The thermal conductivities of Rh₃X are widely distributed in the range 32 to 103 W m⁻¹ K⁻¹ at 300 K; the values converge to around 65 W m⁻¹ K⁻¹ at 1100 K.

The temperature coefficient of thermal conductivity, \( k \), in the temperature range 300–1100 K can be roughly estimated by using the following equation:

\[
k = \left(\frac{1}{\lambda_{300\,\text{K}}}\right)\left(\frac{\partial \lambda}{\partial T}\right) \approx \left(\frac{1}{\lambda_{300\,\text{K}}}\right)\left(\frac{\lambda_{1100\,\text{K}} - \lambda_{300\,\text{K}}}{1100 - 300}\right) \tag{iv}
\]

where \( \lambda_{300\,\text{K}} \) and \( \lambda_{1100\,\text{K}} \) are the thermal conductivities at the temperature indicated by the subscript. The temperature coefficients obtained for Rh₃X are plotted against \( \lambda_{300\,\text{K}} \) in Figure 3. The plots for intermetallic compounds with crystal structures of L₁₂, B₂, and others already reported (18, 19) are also shown in Figure 3, together with data for pure metals (20–22). Note that the data for pure metals in which lattice transformation or magnetic transformation occurs in the temperature range 300–1100 K are excluded. It is well known that the thermal conductivity of h.c.p. metals is anisotropic, so data for polycrystalline materials are adopted for the h.c.p. metals.

The pure metals are generally characterised by having larger thermal conductivities with smaller temperature coefficients, whereas intermetallic compounds have relatively smaller conductivities with larger coefficients. An overall tendency, which can be seen from Figure 3, is that the thermal conductivity and temperature coefficient are inversely correlated in metallic materials. No negative \( k \) is observed for conductivities below 20 W m⁻¹ K⁻¹, whereas above 90 W m⁻¹ K⁻¹ hardly any positive \( k \) is found.

The thermal conductivity of Rh₃Ti is almost equal to those of conventional L₁₂ compounds such as Ni₃Al and Ni₃Ga, whereas the temperature coefficient of Rh₃Ti is much greater. Rh₃Nb, Rh₃Ta and Rh₃Zr are characterised by greater thermal conductivities and negative temperature coefficients. Their thermal conductivities are nearly
equal to that of NiAl, which is well recognised as a compound of high thermal conductivity (4, 16). In addition, a negative temperature coefficient is quite rare among intermetallic compounds, being identified solely in FeTi and Ni3Ti other than Rh3X (X = Zr, Nb, Ta). The thermal conductivities of Rh3V and Rh3Hf are a little smaller than that of NiAl. However, it may be noted that they have relatively larger thermal conductivities among intermetallic compounds.

The thermal conductivity of an intermetallic compound is correlated quantitatively with those of the constituents of the compound through Nordheim’s relation (23). The high thermal conductivities of Rh3X may be partly due to the high thermal conductivity of pure rhodium, the thermal conductivity of which at 300 K is 150 W m⁻¹ K⁻¹.

**Thermal Expansion**

Thermal expansion (ΔL/L) results for Rh3X are shown in Figure 4. All the dilatation curves are a smooth function of temperature, with no sudden slope changes. The curves in Figure 4 reveal that the thermal expansion of Rh3Hf is slightly smaller than those of either Rh3Ti or Rh3Zr over the temperature range 300–1100 K.
The difference in $\Delta L/L$ is less than 10% at any temperature. Also, the data indicate that Rh$_3$Ta has a smaller thermal expansion than those of Rh$_3$V or Rh$_3$Nb. The slope of the curve of $\Delta L/L$ vs. temperature is the coefficient of thermal expansion (CTE). The slight upward curvature in every dilatation curve indicates that the CTE of Rh$_3$X increases with increasing temperature.

CTE values, $\alpha$, for Rh$_3$X at 800 K are summarised in Figure 5, plotted as column heights on the Periodic Table matrix. The smallest CTE is found for Rh$_3$Ta, whereas Rh$_3$V shows the largest. The following inequalities are observed:

$$\alpha[\text{Rh}_3\text{Ti}] > \alpha[\text{Rh}_3\text{Zr}] > \alpha[\text{Rh}_3\text{Hf}] \quad (v)$$

$$\alpha[\text{Rh}_3\text{V}] > \alpha[\text{Rh}_3\text{Nb}] > \alpha[\text{Rh}_3\text{Ta}] \quad (vi)$$

Thus the trend is that the CTE values of Rh$_3$X decrease as constituent X is positioned lower in the Periodic Table. The deviation from stoichiometry has little influence on the CTE values of intermetallic compounds, as demonstrated in NiAl (24–26) and Ni$_3$Al (26). Therefore, a hypothetical CTE value for stoichiometric Rh$_3$Hf with the L1$_2$ single phase is expected to be approximately equal to that of the experimental value for Rh-23.5 at.% Hf.

The CTE values of pure metals are well known to vary inversely with melting points (27). Figure 6 shows the correlation between the CTE at 800 K and the melting points for Rh$_3$X. Data for intermetallic compounds with L1$_2$, B2 and D0$_{19}$ structures, obtained by this group (28), are also shown in Figure 6, together with literature data.
(22, 29) for pure metals. Since the CTE for h.c.p.
metals is usually anisotropic, the CTE data for
polycrystal were adopted for the h.c.p. metals.

In Figure 6, all the plots for pure metals and
intermetallic compounds including Rh₃X fall on a
common curve, irrespective of crystal structure.
The CTEs of Rh₃X are concentrated around $10 \times 10^{-6} \text{K}^{-1}$, approximately equal to that of pure Rh
and two-thirds as great as the CTE of convention-
al intermetallic compounds such as NiAl and
Ni₃Al. From Figure 6, it can be seen that the smaller CTE values for Rh₃X correlate well with the
higher melting points of the compounds.

The interatomic force in metallic materials is
characterised by cohesive energy, $E_{\text{coh}}$, which is the
difference between the potential energy of atoms
in the gas state and that in crystal of the material.
The cohesive energy in an intermetallic compound
is expressed as the sum of the sublimation energy
of the alloy, $E_{\text{sub}}$, and the heat of formation of the
ordered structure, $\Delta H$ (30):

$$E_{\text{coh}} = E_{\text{sub}} + \Delta H \quad (vii)$$

Table II summarises the $E_{\text{coh}}$, $E_{\text{sub}}$, and $\Delta H$ data
for Rh₃X. The $E_{\text{sub}}$ values were obtained from the
data source (31) and the $\Delta H$ values were calculated
from Miedema’s formula (32, 33). For comparison,
Table II also gives data for conventional inter-
metallic compounds. It is apparent that the
cohesive energy of the intermetallic compounds
originates mostly from the sublimation energy rather than from the heat of formation of the ordered structure. The greater cohesive energy of Rh₃X is correlated with the greater interatomic force, resulting in the higher melting points and smaller CTE values of the compounds. The CTE values of Rh₃Nb and Rh₃Ta are particularly small among the Rh₃X compounds, reflecting their greater cohesive energies.

Conclusions

The thermal conductivity and thermal expansion of the L₁₂ intermetallic compounds Rh₃X (X = Ti, Zr, Hf, V, Nb, Ta) were surveyed to evaluate their feasibility as ultra-high temperature structural materials. Thermal properties were measured at temperatures 300–1100 K. Results are summarised as follows:

[i] There is a noticeable trend in the thermal conductivity of Rh₃X, becoming greater if X belongs to Group 5 rather than to Group 4 in the Periodic Table. Thermal conductivity and its temperature coefficient are inversely correlated for metallic materials. Rh₃Nb, Rh₃Ta and Rh₃Zr are characterised by greater thermal conductivities and smaller temperature coefficients; Rh₃Ti by a lower conductivity and a higher coefficient of thermal expansion.

[ii] The dilatation curves for Rh₃X are characterised by slight upward curvature, indicating that the coefficient of thermal expansion (CTE) increases with increasing temperature. The CTE of Rh₃X decreases as constituent X moves downward in the Periodic Table. The smaller CTE values for Rh₃Nb and Rh₃Ta are ascribed to their higher cohesive energies.

Thus, by virtue of their high thermal conductivities and small CTEs, Rh₃Nb and Rh₃Ta are the most suitable of the Rh₃X compounds for ultra-high temperature structural applications.

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In 2003, two papers were published in this Journal celebrating the bicentenaries of the discovery and isolation of rhodium and palladium by William Hyde Wollaston (1766–1828) (1) and of osmium and iridium by his friend Smithson Tennant (1761–1815) (2). A shorter paper on the four discoveries was published in *Chemistry World* (3) and led to a BBC Radio 4 broadcast (4).

Tennant was born in Selby, a town some 30 km south of York. During preparation of the *Chemistry World* paper, I contacted a local historian, Richard Moody, about locating Tennant’s birthplace. My enquiry inspired him to interest Selby Civic Society in persuading the local council to erect a plaque to this eminent son. The chairman of the Society, Philip Milsom, found that Tennant was born at 12 Finkle Street (2) in the centre of Selby, close to the Abbey where he was baptised. The building is now the “Elizabethan” pub, retaining much of its eighteenth century appearance.

Eventually, a blue plaque was erected on the building, and unveiled on 9 November, 2005. It is probably true to say that the papers (1, 2) catalysed this event. This plaque is the only one in the U.K., and possibly in the whole world, to commemorate the discovery of any of the six platinum group metals (pgms).

Although British chemists have discovered twenty elements (a greater number than any other nation) there appears to be only one other plaque in the U.K. to commemorate such a discovery. The other is a Royal Society of Chemistry Historical Chemical Landmark plaque erected at University College, London, in 2004 to commemorate the isolation of the noble gases by Sir William Ramsay.

Clearly, Wollaston also merits a plaque. The house in which he spent the last four years of his life, 1 Dorset Street, Marylebone, London, does bear a plaque, but only to his friend Charles Babbage (inventor of the Analytical Engine) who bought the house in 1829.

**References**

Platinotype Sets Record Price for Photographs

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On 15th February 2006, the world of photographic art was astonished by the sale price of a single photographic print by Edward Steichen (1879–1973): at $2.928M it was more than twice the previous record price paid for any photograph [a]. Steichen’s print, entitled “The Pond – Moonlight”, dates from 1904 and is described as “multiple gum bichromate over platinum”. The print was sold at auction by Sotheby’s Holdings Inc., of New York, to an unidentified private collector [b]. The vendor, The Metropolitan Museum of Art, New York, had recently acquired the print among its purchase of the celebrated collection of the Gilman Paper Company [c].

The ‘Met’ already possessed another print of this image, hence the decision to offer it for sale. A third print is held by The Museum of Modern Art in New York, and was presumably also made from the same negative. This one is entitled “Moonrise – Mamaroneck, New York” (platinum, cyanotype and ferroprussiate print).

The Steichen (Lot 6 at Sotheby’s sale) was not the only platinum metals print for which a price record was broken: on this occasion Lot 11, a palladium print by Alfred Stieglitz (1864–1946) [d], entitled “Georgia O’Keeffe (Hands)”, dating from 1918, realised $1.472M – triple its estimated sale price. This is a record for a Stieglitz work. Another of Stieglitz’s serial portraits of O’Keeffe, a ‘conventional’ silver-gelatin print from 1919 (Lot 13), realised $1.36M. Although Stieglitz began printing this series of portraits in platinum in 1917 [e], he was soon obliged to turn to palladium and silver papers. Platinum had been declared a strategic material during World War I and commercial platinotype paper then became unavailable.

One could speculate how far these extraordinary prices for photographic prints might be attributable to the use of platinum metals in their preparation. However, this question is not easily answered because the perceived value of such objects has several contributory factors.
Enriching the Platinum Tonality

The process of photographic printing in platinum and palladium has been outlined recently in *Platinum Metals Review* [f]. It is clear that this specialist medium demands more handcrafting skills than the usual procedures of silver-gelatin photography [g]. Also, the product can be regarded as an art object and as archivally permanent, thanks to the inertness of platinum. Platinum images provide a vast range of grey monochrome tonality, but this did not satisfy Steichen artistically. A processed platinum print on plain paper of the finest quality is receptive to over-printing using other photographic media, such as ‘gum bichromate’ or cyanotype, and this is what Steichen did.

In the gum bichromate process, an aqueous solution of gum arabic (gum acacia) is used as a viscous binder for the chosen artists’ pigments. It
is mixed with a soluble dichromate before brushing onto the paper. On exposure to light through the re-registered negative, the chromium(VI) is photochemically reduced to chromium(III), which hardens the gum by crosslinking its macromolecular structure, so making it insoluble and trapping pigment proportionally in those regions where the light falls. Excess pigmented gum is removed by washing in water. The whole negative-working process may then be repeated with a different pigment. The platinum tonality is thus enriched by the addition of colour and luminosity. This ‘painterly’ but photographic method, once known as ‘photographite’, is now called gum dichromate.

Artistic Merit and ‘Collectability’

The subtlety and complexity of handcrafted prints, such as Steichen’s, represent a high point in photographic art. However, even given the specialist skills demanded, most of the value so conspicuously attached to them must derive from the status of the artists themselves.

The names of the American photographers, Edward Steichen and Alfred Stieglitz, are prominent in the history of the ‘modernist movement’ in photography, and its battle for recognition as ‘fine art’ [h]. Steichen and Stieglitz co-founded the elite ‘Photo-Secessionist’ circle. Both men, through their exhibitions, fostered an appreciation of the avant-garde, and were seminal figures in art in the USA. Later, Steichen curated the international photographic exhibition “The Family of Man”.

As there are three examples of the Steichen print, it cannot be uniqueness that has raised the price. These factors surely include the size of the image. “The Pond – Moonlight” at around 16 × 20 inches is very large for a platinum print which can only be made by contact-printing. To achieve this a same-sized negative is required, taken either by a gigantic camera, or by enlargement in the darkroom. By contrast, the Stieglitz prints of the time are of more usual dimensions, about 7.4 × 9 inches. In determining the ‘collectability’ of a photograph, the emotional and aesthetic appeal of the image and its subject matter are powerful factors. In this print we have an impressionistic, dark landscape (at a village on Long Island, New York) of a tree-lined reflective pool illuminated by the moon rising between the branches – an evocative example of the romantic pictorial symbolism typical of the modernist genre, and so well suited to the favourite medium of the day – platinotype.

Remarks

[a] The record was held, briefly, by $1.248M paid for Richard Prince’s “Untitled (Cowboy)”, 1989, at Christie’s International of New York on 8 November 2005. This is a colour photograph of part of a 1970s Marlboro cigarette advertisement, and has provoked a deal of post-modernist debate. Previously, the first photograph to surpass the $1M mark, auctioned at Christie’s in 2003, had been a daguerreotype of the Parthenon, Athens, by Joseph-Philibert Girault De Prangey, from the dawn of photography in 1842

[b] The sum includes the buyer’s premium with the ‘hammer’ price

c] The Gilman Paper Company’s Collection contains many historically important platinotypes among its 8500 items; the Company paid $34,000 for the Steichen in 1983

d] Stieglitz studied at the Technische Hochschule, Berlin, in 1884 under the noted photochemist Hermann Wilhelm Vogel


g] In the early twentieth century, commercially made platinum printing paper could still be purchased from William Willis’s Platinotype Company


The Author

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Ruthenium Allenylidene Complexes
A PROMISING ALTERNATIVE IN METATHESIS CATALYSIS

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This paper presents a detailed account of an array of well-defined ruthenium allenylidene complexes as a promising class of metathesis pre-catalysts. This type of ruthenium complex is readily accessible from commercial reagents, induces good to excellent metathesis catalytic activity and selectivity, and shows a great tolerance towards many organic functional groups. By virtue of these beneficial features, ruthenium allenylidene complexes allow synthesis of a wide range of heterocyclic and carbocyclic compounds through ring-closing metathesis (RCM) and enyne metathesis as well as production of specialty polymers by acyclic diene metathesis (ADMET) and ring-opening metathesis polymerisation (ROMP).

Previous papers in this series (1, 2), pointed out that ruthenium indenylidene and vinylidene complexes, 1 and 2, where R is a phenyl (Ph) or a cyclohexyl (Cy) substituent, constitute a convenient alternative to the first generation Grubbs ruthenium alkylidene metathesis pre-catalysts, 3 and 4 (3, 4), used on a large scale in organic (5–9) and polymer syntheses (10–14). Variations in the ligand sphere of the ruthenium atom have been made. These involve mainly the association of certain ancillary ligands, such as N-heterocyclic carbenes (imidazolin-2-ylidene and its saturated derivative), heterocyclic N-donating ligands (pyridine or different N-heterocycles), O- and O,N-chelated ligands (such as phenyl isopropoxy, Schiff-bases), 5 to 12, (R = Ph or Cy, R’ = Ph or Me) (15–31). However, the synthesis of novel metathesis initiators of improved accessibility and with a better application profile is still a challenge to organometallic and metathesis researchers.
The present work is devoted to a vast and promising class of ruthenium metathesis pre-catalysts, derived essentially from neutral and cationic ruthenium allenylidene complexes, 13 and 14, respectively, (R = Ph or Cy, X = PF₆, BF₄, BPh₄, OTf), that gained wide applicability as metathesis initiators due to their easy accessibility and good to excellent catalytic properties.

**Types of Ruthenium Allenylidene Complexes**

The family of neutral and cationic ruthenium allenylidene complexes is very large (32–37) and a considerable number of its members are now recognised as active metathesis catalysts (5, 6, 33).

**Neutral Ruthenium Allenylidene Complexes**

Three neutral, coordinatively unsaturated 16-electron ruthenium allenylidene complexes, of different types, namely the bisphosphane complex 15, the imidazolin-2-ylidene complex 16 and the bimetallic complex 17, have been prepared and evaluated for their catalytic efficacy in alkene metathesis reactions (38, 39).

The bisphosphane complex, 15, is the allenylidene analogue of Grubbs catalyst 3, but with PCy₃ ligands (4). A complex similar to 15 but having PPh₃ groups instead of PCy₃ seems to be rather unstable under normal conditions and rearranges readily to indenylidene, as will be shown in a later section (see p. 84). More stable but less active, the imidazolin-2-ylidene complex, 16, which is the allenylidene analogue of complex 5, stems from complex 15 by simple ligand substitution. The binuclear allenylidene complex, 17, is a highly active metathesis ruthenium complex, and is related to the binuclear benzylidene complex [Ru₂Cl₄(=CHRPh)(p-cymene)(PCy₃)] reported earlier by Grubbs and coworkers (40).

**Cationic Ruthenium Allenylidene Complexes**

Up to now, a vast library of cationic, coordinatively saturated 18-electron ruthenium allenylidene complexes, has been reported (41–48) and many of these have been successfully applied in various alkene metathesis (49) and ring-opening metathesis polymerisation (ROMP) reactions (50). Essentially, the main representatives of this class of allenylidene complexes, for example, complexes 18–21, contain η⁶-arene ligands associated with phosphine and chloride, in conjunction with a ‘non-coordinating’ counterion X⁻.

By varying the substituents at the phosphine (R = Ph, Cy, i-Pr) and allenylidene moieties (R’ = Ph, p-chlorophenyl, p-methoxyphenyl, etc.), and the nature of the counterion X⁻ (X = PF₆, BPh₄, BF₄, OTf, etc.) a great number of this type of ruthenium complex could be conveniently prepared. Due to easy accessibility, their potential as metathesis pre-catalysts has been extensively evaluated. Some of them allowed metathesis reactions to be performed in ionic liquids of the type 1-butyl-3-methylimidazolium salts, as their cationic nature ensured a high solubility of the catalytic species in the reaction medium (51).

Incorporation of imidazolin-2-ylidene as the ancillary ligand in the arene ruthenium allenylidene
complexes, such as 22, provided very active initiators in the ROMP of cycloolefins (52).

Moreover, binding the arene ligand with the dihydroimidazolin-2-ylidene unit through a methylene tether, in a half-sandwich mode, led to the η1:η6-arene-carbene ruthenium allenylidene complex, 23 which was highly active in ring-closing metathesis (RCM) of 1,6-dienes (53). Complex 23 allowed the metathesis of dienes to be selectively directed towards either RCM or cycloisomerisation products.

A structurally different cationic ruthenium allenylidene complex 24, with two phosphines containing hemilabile methoxy groups, has also been reported (54). This bidentate ruthenium complex showed a lower activity in RCM of dienes and ROMP of cycloolefins as compared with the arene ruthenium complex of type 18, but the synthesis and structure of 24 are challenging issues.

Numerous advantages are offered in many applications by the heterogenised version 25 of the arene ruthenium complex 18, obtained through immobilisation on polystyrene (55).

This supported ruthenium pre-catalyst has been reused several times in RCM of dienes, but this was possible only after reactivation in a separate process.

**Miscellaneous Ruthenium Allenylidene Complexes**

The exchange of the triphenylphosphines in [RuCl2(PPh3)3] with water-soluble phosphines, followed by reaction with 3,3-diphenylpropyn-3-ol (in methanol (MeOH)) gave the dimeric ruthenium allenylidene complex 26 which was able to initiate, under certain conditions (protic solvents), ROMP of cycloolefins (56). For instance, in
ROMP of cyclopentene, complex 26 led to considerable polymer yields when, in order to activate the catalytic system, Brönsted acids were used as co-initiators.

A large array of neutral and ionic ruthenium allenylidene complexes, bearing quite diverse ligands and substituents, has been prepared and their catalytic properties in various chemical transformations investigated (57–62). Some of these ligands or substituents might induce asymmetry in the metal complex, generating chiral ruthenium allenylidene catalysts of significance for enantioselective metathesis catalysis.

**Synthesis of Ruthenium Allenylidene Complexes**

**Neutral Ruthenium Allenylidene Complexes**

The neutral, 16-electron ruthenium allenylidene complex 15 was synthesised almost simultaneously by Fürstner and Hill (38), and Nolan and coworkers (39) by reacting [RuCl₂(PPh₃)₃] or [RuCl₂(PPh₃)₄] with commercially-available 3,3-diphenylpropyn-3-ol, followed by PCy₃, see Equation (i).

A similarly straightforward route for synthesis of the PPh₃ analogue (15a) has been reported by Hill and coworkers (63) but subsequent detailed investigation of its structure has proved that the compound is really the ruthenium 3-phenyl-1-indenylidene complex 11, supposedly formed by intramolecular rearrangement of an allenylidene structure, 15a, previously formulated for this complex (39b), see Equation (ii).

Synthesis of complex 15 can also conveniently start from the commercially available ruthenium dimer 27, which reacts with 3,3-diphenylpropyn-3-ol and 2 equivalents of tricyclohexylphosphine. Further substitution of a phosphe group with 1,3-dimesitylimidazolin-2-ylidene readily affords the ruthenium imidazolin-2-ylidene allenylidene complex 16 (39) (Scheme I).

Single-crystal X-ray studies on these two ruthenium allenylidene complexes, 15 and 16, provided significant information about bonding in the solid state and electronic environment at the metal centre (39). Unfortunately, the experimental catalytic activity of complexes 15 and 16 in some ring-closing metathesis of dienes was low, although both complexes are rather stable under the reaction conditions. However, a valuable representative of this group, the...
highly active bimetallic ruthenium allenylidene complex 17, has been prepared in appreciable yield from the same ruthenium dimer 27 and the ruthenium complex 15 (38), see Equation (iii).

This latter complex, 17, has been successfully employed in an array of RCM and enyne metathesis reactions.

**Cationic Ruthenium Allenylidene Complexes**

It is noteworthy that a wide range of cationic 18-electron ruthenium allenylidene complexes, prepared by several research teams using the commercial 3,3-diphenylpropyn-3-ol as the allenylidene moiety source, came as a valuable bonus to state-of-the-art metathesis catalysis (40–47). Thus, a convenient method for synthesis of the ruthenium complex 18a (R = Ph, Cy or i-Pr) is based on the commercially available ruthenium dimer 27, which is first converted to the corresponding monophosphane complex 28 (R = Ph, Cy or i-Pr). The latter, 28, is then reacted with 3,3-diphenylpropyn-3-ol, in the presence of NaPF₆ (or NaBPh₄, etc.) in MeOH at room temperature to give high yields (92–97%) of allenylidene product (49), see Equation (iv).

In the final complex, the sterically encumbered phosphane ligand R₃P prevents further attack of MeOH at the electrophilic α-C atom of the allenylidene group, which would lead to the formation of the Fischer-type carbene complex [(p-cymene)(R₃P)ClRu=CH(OMe)CH=CPh₂] (64).

Several other ruthenium allenylidene complexes, such as 18b (R = Ph, p-chlorophenyl, p-methoxyphenyl, CR₂ = fluorenyle, etc.) could be obtained by a similar method, in aprotic solvents. Thus, on treatment with AgX (X = PF₆, BF₄, OTf, etc.) in CH₂Cl₂, the monophosphane complex 28 forms the rather stable cationic 16-electron complex, 29. The latter compound reacts rapidly with the suitably substituted propyn-3-ol (in CH₂Cl₂ at room temperature) to give the corresponding ruthenium allenylidene complex 18b in appreciable yields (80–95%) (49, 65), see Equation (v).
It is important to emphasise the ready transformation of 18-electron ruthenium allenylidene complexes into their ruthenium indenylidene counterparts, via the allenylcarbyne Ru species, in the presence of strong acids, such as triflic acid (TfOH). In this respect, Dixneuf and coworkers (66) clearly evidenced, by $^{13}$C{1H} and 1H NMR, the generation of the corresponding alkenylcarbyne derivative from complex 18b ($R = Ph, X = OTf$), at –40°C. However, at –20°C the latter intermediate (an alkenyl carbyne derivative) was transformed into the 18-electron arene ruthenium indenylidene complex, 30 (Scheme II).

Remarkably, this ionic, 18-electron arene ruthenium indenylidene complex, arising from the easily-made allenylidene precursor, showed exceedingly high catalytic activity in various metathesis reactions, such as RCM of N-containing dienes (e.g., of N,N-diallyltosyl amide), enyne metathesis (e.g., of N,N-allylpropargyltosyl amide), ADMET (e.g., of 1,8-decadiene) and ROMP of low-strain cycloolefins (e.g., cyclopentene and cyclooctene), even operating at 0°C.

A further variation on these ruthenium complexes consists of the replacement of the $p$-cymene ligand with other arenes, capable of binding coordinatively at the Ru centre, prior to introduction of the allenylidene ligand in the final step. Thus, cleavage of the commercial ruthenium dimer 27 with an aralkyl phosphine, in CH$_2$Cl$_2$ at room
temperature, followed by an intramolecular substitution of the \textit{p}-cymene ligand with the tethered phenyl ring (in chlorobenzene at 140°C) yields the ruthenium complex 31. This intermediate is finally converted, in substantial yields (83–91%), into the new chelated ruthenium allenylidene complex 32, via the above discussed protic or aprotic approach (49) (Scheme III).

The single-crystal X-ray studies of complexes 18a (R = \textit{i}-Pr), 31 and 32 gave, for the first time, interesting data about the structure of these types of complexes and convincingly unravelled the nature of the coordination bonds of the ligands around the ruthenium centre (49).

**Catalytic Properties of Ruthenium Allenylidene Complexes**

Except for a few cases, both families of ruthenium allenylidene complexes, that is: the neutral, coordinatively unsaturated 16-electron and the cationic, coordinatively saturated 18-electron complexes, evidenced good to excellent catalytic activity and selectivity in various metathesis reactions (RCM, ADMET, enyne metathesis, ROMP). By virtue of these catalytic properties and taking into account their easy accessibility from commercial reagents, the class of ruthenium allenylidene complexes holds promise as challenging candidates for productive applications in organic and polymer syntheses. For instance, the neutral, 16-electron ruthenium complex 17 proved to be a highly effective pre-catalyst for RCM of \textit{\alpha,\omega}-dienes and dienynes, at ambient temperature (38). This complex is largely tolerant of functional groups including amide, sulfonamide, bromide, ester, ether, siloxane and fluorenylmethoxycarbonyl substituents. It allows facile and efficient formation of variously functionalised mono- and bicyclic ring systems. Among these compounds, we should mention the structurally complex precursors to exaltolide, a musk odorant, and epilachnene, an insect repellent alkaloid isolated from the pupae of a Mexican beetle.

Syntheses of cyclic compounds via RCM and enyne metathesis using the above binuclear ruthenium allenylidene pre-catalyst are illustrated in Equations (vi) and (vii).

The catalytic performances of the cationic, 18-electron ruthenium complexes of type 14 in RCM of a variety of dienes and in enyne metathesis have been extensively evaluated by Dixneuf and Fürstner (49). The most important finding was that the metathesis activity of these complexes depends essentially on the nature of the phosphane ligand, the remote substituent of the allenylidene moiety and the nature of the “non-coordinating” counterion. For instance, detailed studies on the catalytic activity of cationic complex 14, X = PF\textsubscript{6}, in RCM of N,N-diallyltosyl amide, revealed that when varying the phosphane ligands the catalytic activity decreased in the following order: PCy\textsubscript{3} > \textit{i}-Pr\textsubscript{3} > > PPh\textsubscript{3}, in accordance with
previous observations for the related ruthenium alkylidene pre-catalysts (67). With 14-PF₆ (R = PCy₃) (2.5 mol%) N,N-diallyltosyl amide was quantitatively converted to N-tosyl dihydropyrrole, after 4 h reaction time, in toluene, at 80°C (isolated yield 83%), see Equation (viii).

The above ruthenium pre-catalyst has been applied in RCM of several representative diene substrates allowing synthesis of essentially all ring sizes greater than four, including mono and bicyclic compounds, in good to excellent yields. As expected, the formation of medium sized rings required particularly long reaction times (up to 100 h) and high dilution conditions, while decomposition of the catalytic species seemed to occur with a rate similar to that of the productive RCM. Despite these inherent inconveniences, a large number of heterocyclic compounds pertaining to different heterocyclic systems could also be obtained in good yield (77–88%) by this procedure, see Equations (ix) and (x).

Of great synthetic utility, the complex 14-PF₆ (R = PCy₃) allows efficient synthesis of a set of uncommon macrocyclic compounds; for instance, smooth cyclisations of dienes A and B to the 16- and 18-membered cycloalkenes I and II, respectively, have been successfully achieved by this procedure, see Equations (xi) and (xii).

As just mentioned, compound I is a precursor of the valuable macrocyclic musk, Exaltolide (a
Furthermore, disaccharide III, obtained by cyclisation of the polyfunctional diene C, see Equation (xiii), constitutes an advanced intermediate for synthesis of tricolorin A, a carcinostatic resin glycoside.

A characteristic feature of these ionic catalytic systems is the fact that the counterion exerts a particular influence on the reactivity of the ruthenium allenylidene complex as well as on the selectivity to metathesis products (48). Thus, whereas cation 14, associated with PF₆, BPh₄ or OTf, leads to excellent yields at 80°C, in toluene, its combination with OTf was found to be effective – even at room temperature. This behaviour was tentatively ascribed to the weakly coordinating propensity of the triflate group which may assist the decomplexation process of the p-cymene ligand from the 18-electron allenylidene pre-catalyst and may also
potentially stabilise, in solution, the resulting 14-electron Ru(II) species (49), see Equation (xiv).

Surprisingly, the allenylidene complex 14 having $\text{BPh}_4^-$ or $\text{BF}_4^-$ as counterions is less active and selective, giving rise to numerous side reactions. For instance, with $\text{BF}_4^-$ as the counterion, the ruthenium complex 14 induced cycloisomerisation of $\text{N,N-diallyltosyl amide}$ to methylenecyclopentane (42%), with concomitant cyclisation to N-tosyl dihydropyrrole (31%) and isomerisation to a new diene (18%) (48), see Equation (xv).

Relevant studies on the effect that some additives have on the catalytic activity of the allenylidene complex 14 during N,N-diallyltosyl amide cyclisation pointed out that addition of Lewis or Brönsted acids (e.g., $\text{BF}_3/\text{Et}_2\text{O}$, $\text{HBF}_4/\text{Et}_2\text{O}$, $\text{F}_3\text{CO}_2\text{H}$) increased selectively the RCM activity while almost completely suppressing the above cycloisomerisation. By contrast, ammonium salts (e.g., $\text{n-Bu}_4\text{NF}$) dramatically decreased the overall activity of the complex (49). These interesting observations constitute valuable information for assessing the reaction mechanisms promoted by cationic ruthenium allenylidene complexes.

It is worth noting that allenylidene ligands included in complexes 18 to 20 exert a pronounced influence on the activity of these catalytic systems, and essentially on the selectivity of the reaction products (49). For instance, in the reaction of N,N-diallyltosyl amide discussed above it was possible to alter the catalytic activity of the complex or to switch the reaction pathway from RCM to predominantly cycloisomerisation, simply by varying the distal para-substituents in the phenyl rings of the allenylidene units. This unprecedented result seems to indicate that the allenylidene moiety or a species derived thereof serves as a permanent ligand to the Ru-template throughout the entire catalytic cycle. This behaviour differs fundamentally from that of the parent Grubbs alkylidene complexes 3 and 4, in which the Ru=CHR fragment of the catalyst precursor intervenes only in the initiation process when CHR is cleaved off by reaction with the alkene substrate generating the Ru=CH_2 unit, further responsible for the propagation (68).

Very importantly, ruthenium complex 14 can be photochemically activated efficiently by irradiation with UV light (300 nm), as was found earlier for
the immobilised phosphane complex 25 (R = Cy) (69). Thus, irradiation of a solution of this catalyst and N,N-diallyltosyl amide allows RCM of the unsaturated substrate to proceed in appreciable yield (81%), even at ambient temperature (49), see Equation (xvi).

Such a photochemical activation technique has been successfully applied to a number of enyne substrates which could be conveniently converted into the substituted 3-vinyl-2,5-dihydrofuran derivatives, under these relatively mild conditions (70).

Enyne metathesis, a versatile method for the synthesis of unsaturated bicyclic and polycyclic compounds, has also been effectively performed using the cationic ruthenium allenylidene complex 14. A representative example is the synthesis, in good yield (86%), of 2,2',5,5'-tetrahydro-3,3'-bifuran from the corresponding dienyne using 2.5 mol% complex 14-BF₄⁻, in toluene, at 80°C (48), see Equation (xvii).

Related with the cationic p-cymene ruthenium allenylidene complexes discussed above, the chelated compound 32 (with OTf⁻), containing the tethered phenyl ring instead of p-cymene as the ligand, showed good activity and stability in RCM reactions, allowing synthesis of macrocyclic compounds in appreciable yield, see Equation (xviii).

One of the basic structural parameters for this type of chelated ruthenium complexes, namely the nature of the ‘non-coordinating’ counterion X⁻, was found to play an important part in determining their activity and stability in metathesis reactions.

**Conclusions**

The well defined, neutral and cationic ruthenium allenylidene complexes constitute a new, attractive class of highly effective pre-catalysts for various olefin metathesis reactions. They are easily accessible from commercial reagents, display a wide range of activity and selectivity in metathesis reactions, and show good tolerance towards a large array of functional groups.

This class of ruthenium complexes allows the synthesis of many hetero- and carbocyclic compounds by ring-closing metathesis (RCM) and enyne metathesis as well as production of specialty polymers from cycloolefins by ring-opening metathesis polymerisation (ROMP). Their activity and selectivity can be finely tuned by: suitable variations in the ligand sphere of the metal,
appropriate substitution on the allenylidene moiety and a proper choice of the ‘non-coordinating’ counterion.

Of great significance for practical applications is the observation that the catalytic activity of the cationic, 18-electron ruthenium complexes can be further enhanced by addition of Lewis or Brönsted acids or by irradiation with UV light. Single-crystal X-ray studies unambiguously determined the structures of the neutral, 16-electron, and cationic, 18-electron ruthenium allenylidene complexes and also the defining features of the metal-ligand bonds.

The majority of the ruthenium allenylidene complexes are rather stable at room temperature or upon heating. Compelling proof exists that some ruthenium allenylidene complexes rearrange intramolecularly to the parent ruthenium indenylidene complexes, the latter also displaying high metathesis activity and selectivity. Elegant NMR studies clearly evidenced, for the first time, the transformation of cationic ruthenium allenylidene complexes into the indenylidene congeners via allenylcarbyne ruthenium species.

Overall, the ready accessibility and good to excellent catalytic properties of the well-defined ruthenium allenylidene complexes turn out to be valuable bases for further development and refinement of this class of metathesis pre-catalysts.

References


The Authors

Valerian Dragutan is a Senior Researcher at the Institute of Organic Chemistry of the Romanian Academy. His research interests are homogeneous catalysis by transition metals and Lewis acids; olefin metathesis and ROMP of cycloolefins; bioactive organometallic compounds; and mechanisms and stereochemistry of reactions in organic and polymer chemistry.

Ileana Dragutan is a Senior Researcher at the Institute of Organic Chemistry of the Romanian Academy. Her interests are in sterically hindered amines, syntheses of olefinic monomers via olefin metathesis, stable organic free radicals as spin probes for ESR of organised systems and membrane bioenergetics. She is also interested in transition metal complexes with free radical ligands.
Editor Shun-Ichi Murahashi has brought together 13 chapters written by a range of experts in the field of ruthenium chemistry to produce this book. Each chapter gives a comprehensive account of a particular area of ruthenium-catalysed reactions.

The main body of the work begins with the lengthiest chapter (by M. Kitamura and R. Noyori), detailing hydrogenation and transfer hydrogenation. It is pleasing to find on the opening page a diagram of all the commonly referred to ligands and their abbreviations, which saves the usual frantic search for the definitions every few pages. This chapter, although well set out and organised logically in terms of reaction substrate and selectivity, is rather wordy and would benefit from its text being broken with additional figures.

Oxidation reactions are covered in the next chapter by the editor and N. Komiya. Good use of reaction mechanism schemes makes this account easy to follow without compromising on detail.

The next two chapters deal with carbon-carbon bond formations via ruthenacyle (by Y. Yamamoto and K. Itoh) and π-allylruthenium intermediates (by T. Kondo and T. Mitsudo), respectively. As the chapter titles suggest, the emphasis here is on the synthesis, structure and reactivity of the intermediates. This is complemented by exemplary catalytic reactions and their mechanisms, which are used successfully to illustrate the role of the intermediates in determining the outcomes of the reactions.

Nobel Prize winner R. H. Grubbs and T. M. Trnka contribute a very well written chapter describing ruthenium-catalysed olefin metathesis. This gives a history of the development of the ruthenium catalysts to meet new challenges posed by highly diverse substrates. A good balance is achieved between mechanistic aspects, simple examples, and the use of the catalysts in the synthesis of complex molecules.

A short chapter (by H. Nishiyama) on ruthenium-catalysed cyclopropanation follows. Although this area is dominated by rhodium and copper chemistry, the recent advances in the use of ruthenium catalysts which are becoming viable alternatives, are noted here.

The topics of nucleophilic addition to alkynes and reactions via vinylidene intermediates are tackled by C. Fischmeister, C. Bruneau and P. H. Dixneuf. This material is organised in terms of the nucleophile. Chapter sections decrease in length through O-, N-, P- and Si-nucleophiles, reflecting the relative levels of interest in each area. The use of carbonucleophiles is excluded from this account, but references to relevant recent reviews are given.

Reactions via carbon-hydrogen bond activations that are not covered elsewhere in the book are surveyed by F. Kakiuchi and N. Chatani. The emphasis throughout is on the role of chelation assistance in determining regioselectivity, and good use is made of interesting examples to illustrate the key points.

Ruthenium can also act as a Lewis acid catalyst; reactions where this is achieved by the formation of a σ-bond are described by R. F. R. Jazzar and E. P. Kündig (those using π-bonds are covered elsewhere in the book, although not necessarily labelled as Lewis acid catalysed reactions). Particular attention is paid to stereoselective reactions in this chapter.

A substantial chapter (by T. Mitsudo and T. Kondo) is devoted to ruthenium-catalysed reactions of carbon monoxide and carbon dioxide, reflecting the importance of this topic in industrial and environmental chemistry. A wide range of reactions is considered, from Fischer-Tropsch...
synthesis to numerous carbonylations and CO₂ reductions.

The chapter on ‘Isomerization of Organic Substrates Catalyzed by Ruthenium Complexes’, by H. Suzuki and T. Takao, details rearrangements of alkenes, dienes and enynes, and the racemisation of secondary alcohols. The obvious criticism of this and the previous chapter is that they lack a summary or conclusions; this leaves these subjects at a rather abrupt end.

H. Nagashima briefly discusses ruthenium-promoted radical reactions, concentrating on Kharasch addition, addition of sulfonylchlorides to alkenes and polymer synthesis, before the book is brought to a close with a chapter on bond cleavage reactions.

In the final chapter, S. Koyima and M. Hirano provide an overview of recent advances in carbon-carbon and carbon-hydrogen bond cleavage reactions, but there is no pretence at covering this vast area in detail. Other bond cleavage reactions are omitted.

Overall “Ruthenium in Organic Synthesis” provides a valuable information resource for anyone interested in this area. It is well organised; a comprehensive index allows rapid location of the area of interest. Although the style of writing varies between authors, most create a good balance between illustrative figures and text. For non-specialists in organic chemistry the mechanistic diagrams could be particularly useful. Each chapter constitutes a detailed description of a particular area. The reader is given a sound understanding of how the area has developed to date, and where it is likely to show progress in the future. Further information can be found from the plentiful references at the close of each chapter.

Examples of the applications of ruthenium-catalysed reactions used in industry are tackled to some extent, but I should have liked to see more on practical issues arising from them. Also, comparisons of the utility and performance of ruthenium catalysis with those of other catalysts and methods would have been desirable. While the book is let down by the large number of typographic and other minor errors, which begin to grate when taking it as a whole, nevertheless, a typical reader dipping into this book as reference material will find it rewarding.

The Reviewer

Laura Ashfield joined the Johnson Matthey Technology Centre after completing a doctorate on copper complexes with radiopharmaceutical applications at the University of Oxford. Her current principal interests include the homogeneous catalysis of carbon-carbon coupling reactions used in the synthesis of pharmaceuticals and fine chemicals.
Of the thirty-four known isotopes of palladium, six occur naturally with the following authorised isotopic abundances (2):

<table>
<thead>
<tr>
<th>Isotopic abundance, %</th>
<th>Mass number</th>
</tr>
</thead>
<tbody>
<tr>
<td>102Pd</td>
<td>1.02</td>
</tr>
<tr>
<td>104Pd</td>
<td>11.14</td>
</tr>
<tr>
<td>105Pd</td>
<td>22.33</td>
</tr>
<tr>
<td>106Pd</td>
<td>27.33</td>
</tr>
<tr>
<td>108Pd</td>
<td>26.46</td>
</tr>
<tr>
<td>110Pd</td>
<td>11.72</td>
</tr>
</tbody>
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These naturally occurring isotopes were discovered by Arthur J. Dempster in 1935 (3) at the University of Chicago, Illinois, using a new mass spectrograph made to his design, although only the mass numbers were observed. The actual isotopic abundances were determined for the first time in the following year by Sampson and Bleakney (4).

**Artificial Palladium Isotopes**

In 1935, using slow neutron bombardment, Amaldi et al. (5) identified two palladium activities with half-lives of 15 minutes and 12 hours. The latter value appeared to confirm a half-life of 14 hours that had been obtained earlier that year by McLennan, Grimmett and Reid (6). In 1937, Pool, Cook and Thornton (7) obtained similar half-lives of 18 minutes and 12.5 hours, and Kraus and Cork (8) were able to show experimentally, in that year, that these two activities belonged to $^{111}$Pd and $^{109}$Pd, respectively. Other slow neutron bombardment activities found for palladium, such as a half-life of six hours discovered by Fermi et al. in 1934 (9) and half-lives of 3 minutes and 60 hours discovered by Kurchatov et al. (10) in 1935 do not appear to have been confirmed.

In 1940, Nishima et al. (11) obtained an unspecified activity with a half-life of 26 minutes which is also likely to have been $^{111}$Pd. The actual half-life of $^{111}$Pd is now known to be 23 minutes, so the different values obtained above are probably indicative of calibration problems.

These unspecified activities raise problems concerning the precedence for treating each discovery in this paper. Once the properties of an isotope are established and it is obvious that an unspecified activity must have been due to this particular isotope, then the activity is assigned to that isotope and can be regarded as being “the discovery”. However, using the definition that the primary criterion for discovery is the determination of both the atomic number and the mass number, these unspecified activities are included here only in the Notes to the Table that accompanies the Table of The Discoverers of the Palladium Isotopes.

Literature manuscript dates and conference report dates can be either the actual year of discovery or close to it, so when they are placed in the public domain these dates can be considered as being the “year of discovery”. However, complications arise with internal reports, especially if they represent the actual discovery, since they may not become publicly known until several years later. In these cases the historical date must obviously take precedence over the public domain date. As an
Born in Paris, Irène Curie was the daughter of scientists Pierre and Marie Curie, and therefore it was hardly surprising that she was academically brilliant. She became her mother’s assistant at the Radium Institute, Paris, when only 21 years old and showed excellent aptitude in the use of the laboratory’s instrumentation.

Frédéric Joliot was also born in Paris and in his twenties studied at the major Paris industrial engineering school, the École Supérieure de Physique et de Chimie Industrielle, under the tutelage of the physicist Paul Langevin, a friend of Marie Curie. Langevin suggested that Joliot should be considered for a post at the Radium Institute. Here Joliot met Irène Curie, who he married in 1926, adopting the surname Joliot-Curie.

After Frédéric had carried out major work to improve the sensitivity of the Wilson cloud chamber for detecting charged atomic particles, the Joliot-Curies became interested in the work of the German physicists Walther Bothe and Hans Becker who had noted that strong radiations were emitted when light elements were bombarded with alpha particles. The Joliot-Curies owned the major source of alpha particles available at that time – polonium which had accumulated over many years at the Radium Institute. They used this source to bombard aluminium foil, and found first neutron emission, followed by a long period of positron radiation. They concluded that they had produced a new isotope of phosphorus of mass 30, compared to mass 31 found in natural phosphorus, and that the positron emission represented the decay of this isotope. This is the first example of the production of an artificial radioactive isotope. The discovery was announced in January 1934, and for this work they were awarded the 1935 Nobel Prize in Chemistry. Now, more than seventy years later, there are over 2700 artificial radioactive isotopes.

Like many physicists in the late 1930s the Joliot-Curies carried out research on nuclear fission that eventually led to both the atom bomb and nuclear power. After the war Frédéric convinced the French government to set up its own Atomic Energy Commission and he became its first High Commissioner. Irène succeeded her mother in becoming the Director of the Radium Institute. However, this was the time of the Cold War and Frédéric had strong left-wing political views. In 1950 Frédéric was dismissed from his post. Undaunted, both put great effort into helping to set up a large particle accelerator and laboratory complex at Orsay, south of Paris (Institut de Physique Nucléaire d’Orsay). This is now considered to be one of the major physics institutes in the world.

Irène died in 1956 and Frédéric in 1958, both from diseases related to prolonged exposure to radiation.

Example, Brosi’s discovery of $^{109}$Pd (12, 13) was given in an unpublished internal report dated July 1946 and was not mentioned publicly until its inclusion in the 1948 “Table of Isotopes” (14). Therefore the discovery was not placed in the public domain until 1948, although 1946 is obviously
<table>
<thead>
<tr>
<th>Mass number</th>
<th>Half-life</th>
<th>Decay modes</th>
<th>Year of discovery</th>
<th>Discoverers</th>
<th>References</th>
<th>Notes</th>
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<tbody>
<tr>
<td>91</td>
<td>ps</td>
<td>EC + β⁺ ?</td>
<td>1994</td>
<td>Rykaczewski et al.</td>
<td>17, 18</td>
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<td>92</td>
<td>1.1 s</td>
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<td>Hencheck et al.</td>
<td>19 A</td>
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<td>19 B</td>
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<td>94</td>
<td>9.0 s</td>
<td>EC + β⁺</td>
<td>1982</td>
<td>Kurcewicz et al.</td>
<td>24</td>
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<tr>
<td>95</td>
<td>–</td>
<td>EC + β⁺ ?</td>
<td>–</td>
<td>–</td>
<td>– C</td>
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<tr>
<td>95m</td>
<td>13.3 s</td>
<td>EC + β⁺, IT</td>
<td>1980</td>
<td>Nolte and Hick</td>
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<td>96</td>
<td>2.03 m</td>
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<td>1980</td>
<td>Aras, Gallagher and Walters</td>
<td>27</td>
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<tr>
<td>97</td>
<td>3.10 m</td>
<td>EC + β⁺</td>
<td>1969</td>
<td>Aten and KAPEYN</td>
<td>28</td>
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<td>98</td>
<td>17.7 m</td>
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<td>1955</td>
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<td>29 D</td>
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<tr>
<td>99</td>
<td>21.4 m</td>
<td>EC + β⁺</td>
<td>1955</td>
<td>Aten and De Vries-Hamerling</td>
<td>29 E</td>
<td></td>
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<tr>
<td>100</td>
<td>3.63 d</td>
<td>EC</td>
<td>1948</td>
<td>Lindner and Perlman</td>
<td>32</td>
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<tr>
<td>101</td>
<td>8.47 h</td>
<td>EC + β⁺</td>
<td>1948</td>
<td>Lindner and Perlman</td>
<td>32</td>
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<tr>
<td>102</td>
<td>Stable</td>
<td>–</td>
<td>1935</td>
<td>Dempster</td>
<td>3</td>
<td></td>
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<tr>
<td>103</td>
<td>16.99 d</td>
<td>EC</td>
<td>1946</td>
<td>1. Brosi</td>
<td>12, 13 F</td>
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<tr>
<td>104</td>
<td>Stable</td>
<td>–</td>
<td>1935</td>
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<td>3</td>
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<tr>
<td>105</td>
<td>Stable</td>
<td>–</td>
<td>1935</td>
<td>Dempster</td>
<td>3</td>
<td></td>
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<tr>
<td>106</td>
<td>Stable</td>
<td>–</td>
<td>1935</td>
<td>Dempster</td>
<td>3</td>
<td></td>
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<tr>
<td>107</td>
<td>6.5 x 10⁶ y</td>
<td>β⁻</td>
<td>1949</td>
<td>Parker et al.</td>
<td>34 G</td>
<td></td>
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<tr>
<td>107m</td>
<td>21.3 s</td>
<td>IT</td>
<td>1957</td>
<td>Schindewolf</td>
<td>35 H</td>
<td></td>
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<tr>
<td>108</td>
<td>Stable</td>
<td>–</td>
<td>1935</td>
<td>Dempster</td>
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<tr>
<td>109</td>
<td>13.7012 h</td>
<td>β⁻</td>
<td>1937</td>
<td>Kraus and Cork</td>
<td>8 I</td>
<td></td>
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<tr>
<td>109m</td>
<td>4.696 m</td>
<td>IT</td>
<td>1951</td>
<td>Kahn</td>
<td>38</td>
<td>I</td>
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<tr>
<td>110</td>
<td>Stable</td>
<td>–</td>
<td>1935</td>
<td>Dempster</td>
<td>3</td>
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<tr>
<td>111</td>
<td>23.4 m</td>
<td>β⁻</td>
<td>1937</td>
<td>Kraus and Cork</td>
<td>8 J</td>
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<tr>
<td>111m</td>
<td>5.5 h</td>
<td>IT, β⁻</td>
<td>1952</td>
<td>McNinns</td>
<td>40</td>
<td></td>
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<tr>
<td>112</td>
<td>21.03 h</td>
<td>β⁻</td>
<td>1940</td>
<td>Nishina et al.</td>
<td>11</td>
<td></td>
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<tr>
<td>113</td>
<td>1.55 m</td>
<td>β⁻</td>
<td>1953</td>
<td>Hicks and Gilbert</td>
<td>41</td>
<td></td>
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<tr>
<td>113m</td>
<td>300 ms</td>
<td>IT</td>
<td>1993</td>
<td>Penttila et al.</td>
<td>42 K</td>
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<tr>
<td>114</td>
<td>2.42 m</td>
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<td>1958</td>
<td>Alexander, Schindewolf and Coryell</td>
<td>46</td>
<td></td>
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<tr>
<td>115</td>
<td>25 s</td>
<td>β⁻</td>
<td>1987</td>
<td>Fogelberg et al.</td>
<td>44, 45</td>
<td></td>
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<tr>
<td>115m</td>
<td>50 s</td>
<td>β⁻, IT</td>
<td>1958</td>
<td>Alexander, Schindewolf and Coryell</td>
<td>46 L</td>
<td></td>
</tr>
<tr>
<td>116</td>
<td>11.8 s</td>
<td>β⁻</td>
<td>1970</td>
<td>Aronsson, Ehn and Rydberg</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>117</td>
<td>4.3 s</td>
<td>β⁻</td>
<td>1968</td>
<td>Weiss, Elzie and Fresco</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>117m</td>
<td>19.1 ms</td>
<td>IT</td>
<td>1989</td>
<td>Penttila et al.</td>
<td>49, 50</td>
<td></td>
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<td>118</td>
<td>1.9 s</td>
<td>β⁻</td>
<td>1969</td>
<td>Weiss et al.</td>
<td>51</td>
<td></td>
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<tr>
<td>119</td>
<td>920 ms</td>
<td>β⁻</td>
<td>1990</td>
<td>Penttila et al.</td>
<td>50</td>
<td></td>
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<tr>
<td>120</td>
<td>492 ms</td>
<td>β⁻</td>
<td>1992</td>
<td>Janas et al.</td>
<td>52, 53</td>
<td></td>
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<tr>
<td>121</td>
<td>285 ms</td>
<td>β⁻ ?</td>
<td>1994</td>
<td>Bernas et al.</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>122</td>
<td>175 ms</td>
<td>β⁻ ?</td>
<td>1994</td>
<td>Bernas et al.</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>123</td>
<td>174 ms</td>
<td>β⁻ ?</td>
<td>1994</td>
<td>Bernas et al.</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>124</td>
<td>38 ms</td>
<td>β⁻ ?</td>
<td>1997</td>
<td>Bernas et al.</td>
<td>55</td>
<td></td>
</tr>
</tbody>
</table>

*ps = particle stable; IT = isomeric transition*
**Notes to the Table**

| A | 92Pd | Hencheck et al. (19) only determined the isotope to be particle stable. The half-life was first determined by Wefers et al. in 1999 (20). |
| B | 93Pd | Hencheck et al. (19) only determined the isotope to be particle stable. The half-life was first accurately determined by Schmidt et al. (21) and Wefers et al. (22, 23) in 2000. A preliminary half-life of 9.3 s, determined by Wefers et al. in 1999 (20), was later withdrawn (22). |
| C | 95Pd | The ground state has not been discovered, but Schmidt et al. (25) have suggested that the half-life is probably between 1.7 and 7.5 s from a consideration of the decay characteristics of 85Rh. |
| D | 98Pd | Aten and De Vries-Hamerling (30) first suggested the existence of this isotope in 1953. The discovery was independently confirmed by Katcoff and Abrash in 1956 (31). |
| E | 99Pd | The discovery by Aten and De Vries-Hamerling (29) in 1955 was independently confirmed by Katcoff and Abrash in 1956 (31). |
| F | 103Pd | The unpublished 1946 internal report of Brosi (12, 13) was not made public knowledge until included in the 1948 "Table of Isotopes" (14). Thus, Matthews and Pool appeared to be unaware of it in 1947 and their discovery can be considered to be independent. |
| G | 107Pd | The unpublished 1949 internal report of Parkes et al. (34) was not made public until its inclusion in the 1953 "Table of Isotopes" (15). |
| H | 107mPd | The discovery by Kahn (38) was given in an unpublished 1951 report and was not made public until its inclusion in the 1953 "Table of Isotopes" (15). Flammersfeld (36) observed this isotope in 1952 but could not decide whether or not it was 107mPd or 109mPd. |
| I | 109mPd | Segrè and Seaborg (39) appeared to dispute the discovery by Kraus and Cook (8) since their half-life of 86 m differed significantly from that of 7 m determined by the latter. However Kraus and Cook appear to have definitely identified the 180 h (7.45 d) half-life daughter isotope 111Ag. |
| J | 111Pd | Meikrantz et al. (43) suggested the existence of an isomer of 113Pd with a half-life exceeding 100 s; such an isomer should have been observed by Fogelberg et al. (44) but was not found. |
| K | 113mPd | According to Fogelberg et al. (45), Alexander, Schindewolf and Coryell (46), as with later observations of this isotope, may only have been observing a mixture of the ground state and isomeric state. Therefore the discovery of the pure isomeric state should probably be credited to Fogelberg et al. (44) in 1987. |

**Some of the Terms Used for this Review**

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>the number of protons in the nucleus</td>
</tr>
<tr>
<td>Mass number</td>
<td>the combined number of protons and neutrons in the nucleus</td>
</tr>
<tr>
<td>Nuclide and isotope</td>
<td>A nuclide is an entity characterised by the number of protons and neutrons in the nucleus. For nuclides of the same element the number of protons remains the same but the number of neutrons may vary. Such nuclides are known collectively as the isotopes of the element. Although the term isotope implies plurality it is sometimes used loosely in place of nuclide.</td>
</tr>
<tr>
<td>Half-life</td>
<td>the time taken for the activity of a radioactive nuclide to fall to half its previous value</td>
</tr>
<tr>
<td>Electron volt (eV)</td>
<td>The energy acquired by any charged particle carrying a unit (electronic) charge when it falls through a potential of one volt, equivalent to $1.602 \times 10^{-19}$ J. The more useful unit is the mega (million) electron volt, MeV.</td>
</tr>
</tbody>
</table>
Decay Modes

<table>
<thead>
<tr>
<th>Mode</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Alpha decay is the emittance of alpha particles, which are $^4$He nuclei. Thus the atomic number of the daughter nuclide is lower by two and the mass number is lower by four.</td>
</tr>
<tr>
<td>β⁻</td>
<td>Beta or electron decay for neutron-rich nuclides is the emittance of an electron (and an anti-neutrino) as a neutron decays to a proton. The mass number of the daughter nucleus remains the same but the atomic number increases by one.</td>
</tr>
<tr>
<td>β⁺</td>
<td>Beta or positron decay for neutron-deficient nuclides is the emittance of a positron (and a neutrino) as a proton decays to a neutron. The mass number of the daughter nucleus remains the same but the atomic number decreases by one. However, this decay mode cannot occur unless the decay energy exceeds 1.022 MeV (twice the electron mass in energy units). Positron decay is always associated with orbital electron capture (EC).</td>
</tr>
<tr>
<td>EC</td>
<td>Orbital electron capture. The nucleus captures an extranuclear (orbital) electron which reacts with a proton to form a neutron and a neutrino, so that, as with positron decay, the mass number of the daughter nucleus remains the same but the atomic number decreases by one.</td>
</tr>
<tr>
<td>IT</td>
<td>Isomeric transition, in which a high energy state of a nuclide (isomeric state or isomer) usually decays by cascade emission of $γ$ (gamma) rays (the highest energy form of electromagnetic radiation) to lower energy levels until the ground state is reached. However, certain low-level states may also decay independently to other nuclides.</td>
</tr>
</tbody>
</table>

the proper historic year and must be treated as the actual “year of discovery”.

A technique is used for light and medium-heavy nuclides in which the nuclide fragments from a nuclear reaction are guided into a time-of-flight mass spectrometer.

The atomic numbers and the mass numbers of the detected nuclides can be determined by measuring: the total kinetic energy of the beam, the loss in energy when the beam is injected into an ionisation chamber and the actual time of flight. The determination of these numbers satisfies the criteria of discovery.

For detection in the mass spectrometer, the lifetimes of the nuclides must exceed 500 nanoseconds and must therefore be particle stable. It is expected that particle unstable nuclides, that is those that emit protons for the lighter isotopes of an element and those which emit neutrons for the heavier isotopes, are likely to have extremely short half-lives in this mass region. If, statistically, a nuclide should have been detected by the sensitivity of the technique, but was not, then it is likely to be particle unstable and thus can also satisfy the criteria of discovery, especially if it confirms theoretical predictions. None of the lighter and heavier palladium isotopes discovered by this technique have proved to be particle unstable, so the proton and neutron drip lines have not yet been reached for this element.

Selected half-lives in the Table of ‘The Discoverers of the Palladium Isotopes’ are from the revised NUBASE database (16), except for those of masses 120 to 124 which are from the later measurements of Montes et al. (56). The criteria for discovery are generally those adopted in the review on platinum (1).

References
Nitrous Oxide Greenhouse Gas Abatement Catalyst

Among the naturally occurring greenhouse gases, nitrous oxide (N\textsubscript{2}O) is estimated to absorb 310 times more heat per molecule than carbon dioxide, thus contributing substantially to global warming (3). Atmospheric N\textsubscript{2}O is estimated to have increased by ~16% since the Industrial Revolution, and has contributed 6 to 11% to enhancing the greenhouse effect. Up to 40% of total atmospheric N\textsubscript{2}O is estimated to be man-made – equivalent to ~15 million tonnes per year (4). N\textsubscript{2}O is gradually accumulating in the atmosphere (2), despite slow breakdown by sunlight.

To reduce the production/emission of N\textsubscript{2}O as a waste product from nitric acid plants, the Norwegian nitrogen fertiliser manufacturer Yara International ASA (5) has developed a N\textsubscript{2}O abatement catalyst based on the reaction:

\[ 2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2 \]

The de-N\textsubscript{2}O catalyst, which can cope with the high temperatures and corrosive environment of a nitric acid plant, is placed under the rhodium-platinum gauze pack and the catchment gauzes (6). It enables the N\textsubscript{2}O output in most plants to be reduced by 80% or more. The catalyst is of pelleted configuration, and when used with the Pt-Rh catalyst system gives an environmentally enhanced process with highly efficient N\textsubscript{2}O abatement. The catalyst is installed in several nitric acid plants, and more are planned.

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References
2 “Data by gas – N\textsubscript{2}O without LULUCF”, http://ghg.unfccc.int/tables/a2n2owo_lulucf.html
5 Yara, http://www.yara.com/

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ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES
Surface Oxides and their Effect on the Oxidation Behavior of Amorphous and Nanoquasicrystalline Zr-Pd and Zr-Pt Alloys
The oxidation of melt-spun Zr_{60}Pt_{30} (1) and Zr_{55}Pd_{15} (2) with a nanoquasicrystalline phase embedded in an amorphous matrix has been investigated isothermally as well as nonisothermally in static air. XRD and SEM were used to study the oxides formed. For (1), the kinetics of oxidation is sluggish compared to (2), which is due to the strong interaction between Zr and Pt atoms.

Determination of Hydrogen Absorption Isotherm and Diffusion Coefficient in Pd_{81}Pt_{19} Alloy
Permeation and impedance techniques (1) were used to study H absorption into Pd_{81}Pt_{19} foil. The total amount of H absorbed is smaller than in pure Pd, and the absorption plateau is obtained at negative overpotentials. The H diffusion coefficient was determined by various (1). (1) gave similar values with the exception of the small differential step permeation technique and electrochemical impedance spectroscopy in the transmissive mode. H-induced stress might cause the deviations observed.

Thermodynamic Assessment of the Hf–Os System
The Hf–Os system was assessed by the CALPHAD technique. A three-sublattice model (Hf, Os)0.5(Hf, Os)2 by a single Gibbs energy function. The intermetallic compound HfOs. Using this model, the ordered B2 and second sublattices, respectively.

CHEMICAL COMPOUNDS
Mono- and Di-nuclear Platinum(II) Complexes Containing O- and N-Bonded Acetamide
The preparation and interconversion reactions of novel O- and N-bonded acetamide and deprotonated N- and N,O-bonded acetamido derivatives of Pt(II)-terpy are reported. [Pt(MeCN)(terpy)](OTf)2 was used as the precursor for the O-acetamide derivative. The X-ray structures of the mononuclear N-acetamido and dinuclear N,O-acetamido species were determined.

Synthesis and Characterization of the Nitrides of Platinum and Iridium
High-pressure and high-temperature synthesised Pt nitride (1) of stoichiometry PtN₂ has a large bulk modulus. A structure that is isosctructural with pyrite was proposed for (1). A recoverable nitride of Ir (2) was also synthesised under similar conditions. Although (2) has the same stoichiometry as (1), (2) exhibits much lower structural symmetry. The bulk modulus of (2) is also very large.

Novel Acyclic Carbene-Substituted Phospha-Palladacycles
The synthesis of a phospha-palladacycle substituted with an acyclic carbene, without reduction of the Pd(II) complex, has been achieved for the first time. The reaction of bis(dialkyl)amino carbenes with the very stable phospha-palladacycles leads to metastable η¹-carbene complexes. The latter can be converted by intramolecular reduction to Pd(0) complexes.

Tetrazolecalix[4]arenes as New Ligands for Palladium(II)
The synthesis of bis- and tetrakis-tetrazole derivatives of a calix[4]arene (1) and the structural characterisation of a calixarene containing 4 tetrazole groups at the upper end of a macrocycle and its complex with PdCl₂ were carried out. The tetrazole ligating groups are at the upper rim of (1) to give (1) their bowl shape. (1) can be used in self-assembled cage structures having transition metal cations as linkers.

PHOTOCONVERSION
Synthesis and pH-Sensitive Luminescence of Bis-terpyridyl Iridium(III) Complexes Incorporating Pendent Pyridyl Groups
Three new series of pyridyl-appended bis-terpyridyl Ir complexes (1) are luminescent at room temperature, with long luminescence lifetimes in the µs range in air-equilibrated aqueous solution. The emission intensity and lifetimes of (1) are sensitive to the protonation state of the pyridyl group. Emission may be either quenched or augmented according to the structure of the ligand in (1).
A New Family of Ruthenium(II) Polypyridine Complexes Bearing 5-Aryltetrazolate Ligands as Systems for Electrochemiluminescent Devices
Mono- and dinuclear Ru-polypyridyls containing 5-aryltetrazolates were prepared. Spectroscopic studies of the uncoordinated tetrazolate ligand and complexes highlighted good luminescence efficiency and poor bridge-mediated electronic communication between the metal centres of the dinuclear complexes (1). For one of (1), a very high ECL efficiency was observed.

SURFACE COATINGS
Effect of Thermally Grown Oxide (TGO) Microstructure on the Durability of TBCs with PNiAl Diffusion Bond Coats
The effect of preoxidation surface treatments on Pt-modified NiAl bond coats and electron beam deposited thermal barrier coatings (TBCs) has been studied. The formation of a surface oxide having a coarse-grained columnar structure during the preoxidation process enhanced the TBC performance. Increased TBC durability was consistent with a slower oxide growth rate during exposure of the TBC to high-temperature, cyclic conditions. An oxide microstructure having fewer grain boundaries was achieved by preoxidising the bond coat prior to TBC deposition at an intermediate partial pressure of O2.

Processing TiPdNi Base Thin-Film Shape Memory Alloys Using Ion Beam Assisted Deposition
Thin films of TiPdNi (1) were processed using ion beam assisted deposition (IBAD). As-deposited (1) were found to be amorphous. Postdeposition annealing caused decohesion and delamination. IBAD with in situ heat treatment gave fully martensitic films 1.5 µm thick and with reduced grain size and film defects. (1) can be used in MEMS microactuator applications.

APPARATUS AND TECHNIQUE
Self-Aligned Platinum-Silicide Nanowires for Biomolecule Sensing
The immobilisation of a single-stranded capture DNA onto a Pt-silicide 40 nm nanowire (1) was verified by a fluorescence-labelling technique. A field-effect transistor can distinguish the complementary, mismatched, and denatured DNA via the conductance difference. (1) can sense the minimal target DNA concentration down to 100 fm, and the signal is still 1000-fold larger than the noise signal.

Pd/Porous-GaAs Schottky Contact for Hydrogen Sensing Application
Pd/GaAs (1) and Pd/porous-GaAs (2) Schottky diode sensors were fabricated and characterised using forward and reverse I–V measurements in response to H2 at different temperatures. (1) exhibited low sensitivity to H2. The detection limit of (1) was improved by poring the GaAs wafer using electrochemical HF etching, followed by depositing a Pd layer on its surface to give (2). (2) exhibited sensitivity three times that of (1), with a response time of 1 s for 500 ppm H2.

The Electroanalytical Detection of Hydrazine: A Comparison of the Use of Palladium Nanoparticles Supported on Boron-Doped Diamond and Palladium Plated BDD Microdisc Array
Both a random distribution of Pd nanoparticles supported on a B-doped diamond (BDD) electrode (1) and a Pd plated BDD micro electrode array (2) provide a sensing platform for the electroanalytical detection of hydrazine. (1) has a sensitivity and limit of detection of 60 mA mol–1 L and 2.6 µM, while (2) gives 8 mA mol–1 L and 1.8 µM, respectively. The random Pd distribution in (1) leads to clumps of Pd nanoparticles that effectively act as microelectrodes.

HETEROGENEOUS CATALYSIS
NOx Storage and Reduction on Pt/Alumina Catalysts: Effects of Alkaline-Earth and Rare-Earth Metal Additives
Pt/Al2O3 catalysts (1), modified with alkaline-earth or rare-earth metal oxides, were prepared by incipient-wetness impregnation. The performance and durability of NOx storage of (1) were studied under a lean-burn/rich-burn cycle process. The Ba-promoted (1) had better storage capability and duration, while the Ce-promoted (1) had a higher NO storage capability. (1) containing both Ba and Ce demonstrated high NO storage/conversion. The best operating temperature range was 350–400°C.

The Influence of Fuel Type on Carbon Deposition over Precious Metal Containing Motorcycle Catalysts
The influence of fuel type on C deposition over Pt and Pd containing motorcycle catalysts was studied. MTBE blended gasoline gave carbonaceous species in the form of CxHy, whereas for blended EtOH fuel the species are CxHyO. The majority of the carbonaceous species are deposited on the Pt and Pd sites. FTIR confirmed aromatic rings, alkyl groups and their partial oxidation products in the C deposits.
Washcoating Method for Pd/γ-Al₂O₃ Deposition on Metallic Foams


A method (1) for coating open celled metal foams with a Pd-Al₂O₃ thin layer (20 μm thick) was developed. A sol–gel of pseudoboehmite as a precursor of γ-Al₂O₃ was used to fill the porous structure by percolation. This was activated with Pd using wet impregnation. In an alternative method (2), dry impregnation of γ-Al₂O₃ with Pd was performed and a slurry was prepared (+ H₂O/HNO₃). The slurry was deposited by percolation through the foam structure. Both (1) and (2) produced highly active foams, resulting in light-off temperatures for catalytic CO oxidation of 175–250°C. CO conversions with (1) were > (2), indicating (1) gave more uniform coating.

Hydrogenation of Plant Sterols over a Polymer Fiber-Supported Pd Catalyst


The hydrogenation of a wood-based plant sterol mixture, β-sitosterol, β-sitostanol, campesterol and campestanol, was investigated using a Pd/poly(acrylic acid) grafted polyethylene fibre catalyst (1). Metal species were not leached into the reaction mixture, and mechanical agitation did not damage (1). The scale-up of the hydrogenation process was successfully carried out in pilot-plant and industrial reactors.

Catalytic Autoignition of Higher Alkane Partial Oxidation on Rh-Coated Foams


Steady-state production of syngas (CO and H₂) was attained within 5 s after admitting large alcanes and air into a short-contact-time reactor by using an automotive fuel injector and initially preheating the Rh-coated foam catalysts (1) above the respective catalytic autoignition temperature for each fuel. Minimum catalytic autoignition temperatures on (1) were ~ 260°C for i-octane and 240°C for i-octane and n-decane. In contrast, catalytic autoignition of n-hexadecane indirectly occurred at > 220°C because exothermic homogeneous chemistry had preheated (1) by 30–60°C to ~ 280°C.

Homogeneous Catalysis

 Palladium-Catalyzed Addition of Alkynes to Cyclopropanes


Pd(OAc)₂/[(Me)₂P]BF₄/Er₂N was investigated for the addition of 4-pentyn-1-ol to 3,3-diphenylcyclopropane. The cyclopropane ring remained intact to provide an alkynyliccyclopropane. The active Pd–phosphine complex is generated in situ. Coupling of alkynes and cyclopropanes can thus be used for synthesis of alkynyliccyclopropanes under mild conditions.

Industrial-Scale Palladium-Catalyzed Coupling of Aryl Halides and Amines—A Personal Account


The Pd-catalysed coupling of amines and aryl halides or aryl alcohol derivatives has progressed from a laboratory small-scale transformation into a general, efficient and robust reaction over the last ten years. Applications of this method from an industrial viewpoint, including phoshane ligand synthesis and synthesis of arylpiperazines, arylhydrazines and diaryl-amines, are described. The issues of scale-up and safety are included. (33 Refs.)

Environmentally Friendly Synthesis of Biaryls: Suzuki Reaction of Aryl Bromides in Water at Low Catalyst Loadings


Pd(DPPF)Cl₂ has been shown to be an extremely active catalyst for the Suzuki coupling reaction of aryl bromides in H₂O. This procedure gave biaryls in excellent yields and high TONs (TONs ≤ 870,000 for the reaction of 1-bromo-4-nitrobenzene and phenylboronic acid). A 20% aqueous PEG-2000 solution as the reaction media allows this catalytic system to be readily recyclable for three runs.

Simple and Economical Conversion of Organic Compounds with H₂O₂ Catalyzed by Ruthenium (III) Chloride


Aromatic aldehydes, hydrocarbons, cyclohexanol and benzyl alcohol, dissolved in acetic acid, were oxidised in quantitative to moderate yields by 50% H₂O₂ in the presence of traces of RuCl₃ (1) (~ 10⁻⁶ mol). Conditions for highest yields were obtained. Higher concentrations of (1) decreased the yield. Oxidation in the aromatic aldehydes was selective at the aldehydic group only, and other groups remained unaffected. The extent of oxidation in phenanthrene depends on temperature or the relative amount of substrate or both. It is proposed that the oxo-centred carboxylate species of Ru(III) catalyses the oxidation.

A Simple and Practical Phase-Separation Approach to the Recycling of a Homogeneous Metathesis Catalyst


An efficient new strategy for homogeneous Ru-catalyst phase-separation and recovery which provides products of excellent purity with low Ru content has been designed. An araneone-derived Ru carbene olefin metathesis catalyst (1) exhibited high reactivity and was easily separated after reaction by deposition on silica gel. (1) was reused up to nine times without needing fluorous solvents or special silica gel.
Bifunctional Transition Metal-Based Molecular Catalysts for Asymmetric Syntheses
A chiral bifunctional Ru catalyst (1) that was originally developed for asymmetric transfer hydrogenation of ketones and imines, has been applied to the enantioselective C–C bond formation reaction. The deprotonation of 1,3-dicarbonyl compounds with chiral amido Ru complexes leading to amine Ru complexes bearing C- or O-bonded enolates, followed by further reactions with electrophiles gives C–C bond formation products. (1) has the potential for stereoselective molecular transformation including enantioselective C–H, C–C as well as C–O and C–N bond formation.

FUEL CELLS
Single-Wall Carbon Nanotubes Supported Platinum Nanoparticles with Improved Electrocatalytic Activity for Oxygen Reduction Reaction
Films of Pt/single wall C nanotubes (SWCNTs) cast on a rotating disk electrode exhibit a lower onset potential and a higher electron-transfer rate constant for O reduction, when compared to a Pt/C black catalyst. Improved stability of the SWCNT support is confirmed from the minimal change in the O reduction current during repeated cycling over 36 h. Pt/SWCNT may be used as DMFC and PEMFC cathodes.

Characterization of Electrode Structures and the Related Performance of Direct Methanol Fuel Cells
An increase of ~ 25% in power performance was claimed to be achievable by controlling the pressure of the hot press in the MEA fabrication process for a given Pt loading. The improved performance of the MEA was attributed to the porosity of the cathode in which a network of macrofissures and sub-microfissures allows air to penetrate the cathode. The specific power density was found to almost double when the total porosity increased from 57% to 76%.

Electrocatalytic Activity of Ordered Intermetallic PtSb for Methanol Electro-Oxidation
Ordered intermetallic PtSb (1) was prepared by arc-melting followed by sintering. The electrooxidation of MeOH on (1) was investigated at room temperature by CV and chronoamperometry. (1) was catalytically more active than a polycrystalline Pt electrode surface according to the onset potential and current density.

Template Synthesis of Arrays of Nano Fuel Cells
Pt-Cu nanowires were electrodeposited inside the cylindrical pores of an Anodisc filter membrane. The filter was then soaked in fuming HNO3 to remove the Cu and construct an array of porous Pt electrodes (1). An array of nano fuel cells (2), each ~ 200 nm in diameter, was produced by utilising two arrays of (1) with a polymer electrolyte membrane or an electrolyte support matrix sandwiched between. (2) using aqueous NaBH4 fuel gave power densities of ~ 1 mW cm–2.

Methanol-Tolerant Oxygen Reduction Electrocatalysts Based on Pd-3D Transition Metal Alloys for Direct Methanol Fuel Cells
Pd-based alloys (1), Pd-Co, -Ni and -Cr, have been developed as MeOH-tolerant O reduction electrocatalyst (2). (2) were fabricated by RF sputtering. The electrochemical characteristics of (2) for the ORR were determined in H2SO4 solution with and without MeOH at 30°C. (1) showed a higher ORR electrocatalytic activity than Pd, although lower than Pt. (1) also had no electrocatalytic activity for MeOH oxidation. The maximum electrocatalytic activities for ORR were observed for an alloy composition of ~ 60 at.% Pd in (1).

ELECTRICAL AND ELECTRONIC ENGINEERING
Oriented Self-Assembly of Cubic FePt Nanoparticles
Attempts were made to synthesise single crystalline FePt nanoparticles (1) with cubic shapes. Particles with shapes that are close to cubic or rectangular were obtained. When deposited on surfaces these particles assemble with local order and a square lattice; they orient themselves with their [100] axes perpendicular to the surface and with local interparticle alignment of the [010] and [001] axes oriented parallel to the surface. These FePt nanocube films begin to overcome obstacles associated with magnetic data storage media based on self-oriented magnetic arrays of (1).

MEDICAL USES
The Chemistry of Dinuclear Analogues of the Anticancer Drug Cisplatin. A DFT/CDM Study
A combined DFT/CDM approach was used to study the formation mechanism of dinuclear Pr(II) μ-hydroxo complexes from cisplatin hydrolysis products, their interconversion, decomposition, and reactions with biomolecules. The results are reported to: (i) help assess if dinuclear metabolites play a role in cisplatin chemotherapy, and (ii) elucidate the toxicity and pharmacological inactivity of [cis-{Pr(NH3)2(μ-OH)}2]2+. 
NEW PATENTS

ELECTRODEPOSITION AND SURFACE COATINGS
Enhanced Alloy Compositions for Sputter Targets
HERAeus INC  U.S. Appl. 2005/274,221
A sputter target comprising Co; (in at.%) 0–24 Cr, 0–20 Pt, 0–20 B, 0–10 Au; one of the elements W, Y, Mn, Mo; and 0–7 at.% of an element selected from Pd, Rh, Ir, Ru, Ti, V, Zr, Nb, Hf and Ta. When manufacturing a magnetic recording medium, at least an initial thin-film data storage layer is sputtered over a substrate from the sputter target.

Nucleation and CVD of PGM Films
MICRON TECHNOL INC  U.S. Appl. 2006/014,367
A method of depositing a film (1) of Pt, Rh, Ir or Ru metal by CVD includes bubbling a non-reactive gas through an organometallic precursor (2) to transport vapourised (2) to a deposition chamber. (1) is deposited onto a non-silicon bearing substrate (3) under UV light. (1) is then annealed in an O2 atmosphere at low enough temperature to avoid oxidation of (3). The resulting (1) is free of silicide, consistently smooth, and has good step coverage.

Semiconductor Gas Sensor
FIS INC  World Appl. 2006/011,202
A gas sensor with improved sensitivity and responsiveness is provided with a metal oxide semiconductor element (1). The electrical resistance of (1) alters on sensing a gas to be detected. A metal oxide insulator holding at least Pt or Pd is dispersed in (1). Adverse effects of Pt and Pd on (1) are suppressed. Operation of the inner part of the element is thus entirely catalysed by Pt and Pd.

HETEROGENEOUS CATALYSIS
Exhaust Gas Purifier and Method of Purification
HONDA MOTOR CO LTD  World Appl. 2005/121,517
A technology for removing NOx in exhaust gas from a stoichiometric combustion gasoline engine can also remove NOx from O-rich exhaust gases such as those from diesel engines. The catalyst (1) is Pd oxide supported on LnAlO3. H2 is fed into the exhaust gas from a supply unit upstream of the catalytic converter. (1) is highly reactive with NOx, even with O present, giving a high depollution ratio.

Catalytically Coated Particle Filter
UMICORE AG & CO KG  World Appl. 2006/021,337
A catalytically coated particle filter (1) comprises two sequential catalysts. The first Pd/Pt catalyst (2) is in the gas inlet zone of (1). The second catalyst (3) is located behind (2) and preferably contains only Pt as the catalytically active component. (2) and (3) impart good resistance to ageing and sulfur poisoning to (1).

Hydrogenation of Methyleneedianiline
AIR PRODUCTS CHEM INC  U.S. Appl. 2006/047,173
A crude methyleneedianiline feedstock (1) is pretreated and partially hydrogenated by passing over a Ru catalyst on a fixed bed support. (1) is cooled without venting H2 gas and solvent vapour. Pretreated (1) is then ring-hydrogenated in a batch reaction over a Rh or mixed Rh/Ru catalyst carried on a monolith support incorporating a washcoat.

Exhaust Gas Cleaning Catalyst with Oxygen Occlusion Material
MAZDA MOTOR CORP  Japanese Appl. 2005-279,332
An exhaust gas cleaning catalyst consists of a catalytic layer formed on the cell walls of a honeycomb base containing Al2O3. The catalytic layer contains Pd and an O occlusion material (1), which is a multiple oxide containing Ce, Zr and K. Exhaust gas cleaning performance is enhanced by the O occluding/releasing properties of (1).

Catalyst for Purifying Exhaust Gas
TOYOTA MOTOR CORP  Japanese Appl. 2005-279,435
A ZrO2 catalyst carrier (1) supports Rh and contains a lanthanide element. The crystal lattice of Rh conforms to that of (1). The affinity of Rh particles (2) for (1) is enhanced by this method. (2) are stabilised, remain immobile, even at high temperatures, and the grain growth of (2) is inhibited. The catalyst is manufactured by adding an acid solution of a Rh compound to an aqueous solution of a basic lanthanide salt in which ZrO2 powder is dispersed.

Toxic Gas Oxidation Catalyst
KOREA RES INST CHEM TECHNOL  Japanese Appl. 2005-305,403
Active Pt, Pd and Cu ions are deposited with uniform distribution on a solid porous carrier to produce a catalyst (1). Toxic gases such as CO, SO2, CH3CHO and NH3 are removed effectively by a low-temperature oxidation reaction using (1). (1) has a long lifetime even when the toxic gas contains moisture. Applications include air cleaning for indoor environments and industrial sites producing pollutants.

HOMOGENEOUS CATALYSIS
Process for Making Haloorganosiloxanes
GENERAL ELECTRIC CO  World Appl. 2005/118,598
A haloorganosiloxanes is prepared by reacting an olefinic halide with an alkoxysilane in which the alkoy group(s) contain at least two C atoms. The reaction medium contains a Ru-containing catalyst and an electron-donating aromatic compound promoter. The process can be used to prepare, among other things, chloropropyltriethoxysilane, a key intermediate in the manufacture of silane coupling agents.
Process for Forming an Aromatic Amine Compound

**EASTMAN KODAK CO**  
*World Appl. 2006/011,879*

An aromatic amine product is formed by combining an aromatic primary or secondary initial amine with an aromatic halide compound in the presence of a Pd complex and a phosphine compound catalyst to form a mixture (1); heating (1) to a first temperature of at least 60°C; and adding a base material to the heated mixture. The temperature of the mixture is maintained at or above the first temperature for sufficient time to form as a product an aromatic substituted form of the aromatic primary or secondary initial amine. The process provides products of high purity in good yields.

Direct Oxidation of Methane to Acetic Acid

**BP CHEMICALS LTD**  
*U.S. Appl. 2006/025,628*

CH3COOH is produced by oxidising CH4 with an O2-containing gas in the presence of either concentrated or fuming H2SO4, a Pd-containing catalyst (1) and a promoter, preferably a Cu or Fe salt. Adding a promoter and O2 to a system containing (1) (for instance, PdCl2) increases the rate of formation of CH3COOH from CH4 by more than an order of magnitude as compared with previous methods. The precipitation of Pd black is also inhibited.

Continuous Hydrocracking of Polyester

**MITSUBISHI GAS CHEM. CO INC**  
*Japanese Appl. 2005-296,826*

A method for the continuous hydrocracking of polyesters to produce alcohols is claimed. The reaction solvent (1) and a Ru complex catalyst (2) with 1,1,1-tris(diphenylphosphino)methyl ethane as a ligand are separated from the reaction mixture by distillation. An organic solvent is added to the distillation residue to separate and recover (2). Both (1) and (2) are reused.

Production of Optically Active Alcohols

**KAWAKEN FINE CHEM. CO LTD**  
*Japanese Appl. 2005-298,411*

A prochiral carbonyl compound (especially one containing an amino group) undergoes asymmetric hydrogenation in the presence of a Rh complex or a Ru complex containing a phosphine compound catalyst to form an optically active alcohol is produced at a practical reaction rate and in high enantiomeric excess.

FUEL CELLS

Stabilisation of Power Generation

**TOYOTA MOTOR CORP**  
*Japanese Appl. 2005-276,526*

Pt catalyst is supported at the inner walls of conductive porous C tubes in a F ion exchange resin film. This configuration improves the discharge of H2O produced by the reaction in a fuel cell which would otherwise cause a drop in power generating performance in areas of high current density. Power generation is stabilised at high voltage and high current by enhancing the efficiency of the cell reaction.

Electrode Resistant to Freezing Damage

**NISSAN MOTOR CO LTD**  
*Japanese Appl. 2005-302,434*

An electrode paste is manufactured by mixing, agitating, and vacuum deaerating a C particulate carrying Pt (1), a different C particulate (2) of smaller particle size carrying no Pt, and a solution of a perfluorosulfonic acid polymer system of low molecular weight having H ion conductivity. By this process, the micropores of (1) are closed by (2), thus protecting the electrode from damage by freezing and expansion of H2O.

Platinum-Ruthenium Alloy Catalyst for DMFC

**HITACHI MAXELL LTD**  
*Japanese Appl. 2005-324,156*

A Pt-Ru alloy catalyst is manufactured in stages. C powder is dispersed in an organic solvent composed of at least one kind of alcohol and a Pt chloride and a salt or complex of Ru is then dissolved in the dispersion. The pH value of the alcohol solution is adjusted to the range of 9 to 10. Lastly the solution is heated under reflux in an inert atmosphere.

CHIMICAL TECHNOLOGY

Iridium Recovery from Waste Solution

**TANAKA KIKENZOKU KOGYO KK**  
*Japanese Appl. 2005-298,240*

An alkali metal hydroxide is added to a waste solution (such as a plating solution) containing an Ir-halogen complex to recover Ir as Ir(OH)4 (1). (1) is suspended in water. HCl or HBr is added, followed an alkali metal halide to obtain an Ir-alkali metal complex (2). (2), obtained at high yield in high purity, is suitable for processing into Ir metal or fresh plating solution.

ELECTRICAL AND ELECTRONIC ENGINEERING

Hard-Bias Design for Extra-High Density Recording

**HEADWAY TECHNOLOG INC**  
*U.S. Appl. 2005/275,975*

A hard-bias structure for biasing a free layer in a magnetoresistive element within a read head comprises a composite hard-bias layer of configuration Co78.6Cr5.2Pt16.2/Co65Cr15Pt20. The upper Co65Cr15Pt20 layer has a larger Hc value and a thickness > 2 times that of the Co78.6Cr5.2Pt16.2 layer. The magnetic moment of the hard-bias structure may be enhanced by a b.c.c. underlayer such as FeCoMo. Optionally, there is no Co78.6Cr5.2Pt16.2 layer and the Co65Cr15Pt20 layer is formed on the b.c.c. underlayer.

MEDICAL USES

Molecular Markers for Cisplatin Resistance

**RES. DEVELOPMENT FOUNDATION**  
*U.S. Appl. 2006/019,268*

Diagnostic and/or prognostic methods involving a collection of differentially expressed genes may be used to identify resistance (1) to the therapeutic effect of the Pt-based drug cisplatin in human ovarian cancer. The method includes the identification and use of markers for (1).
Sulfur as a Catalyst Poison

Precious metal catalysts are crucial to the operation and economics of many hydrocarbon processing applications. Feedstock poisons impair the performance of a catalyst by reducing its activity, either via competitive adsorption onto active sites, or by alloy formation with active platinum group metal (pgm) sites. More stringent removal of harmful contaminants from hydrocarbon feedstocks is therefore essential to achieve the highest catalytic activity/selectivity, and an acceptable cycle length.

Several potential poisons are encountered in process streams. A major problem for catalyst suppliers is that plant operators often cannot supply a detailed analysis of the stream to be treated. Another issue is the accuracy needed to measure process contaminants which may be almost undetectable. These low level poisons gradually accumulate on the surface of a pgm catalyst, causing an inexorable decline in its activity/selectivity.

Poisoning can generally be classified as either reversible (temporary) or irreversible (permanent). After temporary poisoning, catalytic activity can be largely recovered by removing the poison source or by adequately cleaning the catalyst surface by air oxidation and/or steaming. The irreversible effect of permanent poisons is due to their being so strongly adsorbed that they cannot be adequately removed. Loss in catalyst activity often includes reduced cycle length, increased pressure drop in the reactor and increased carbon deposition.

Sulfur (S) species (H₂S, RSH, RSSR…) are poisons (1) for all catalytic processes employing reduced metals as the primary active phase. They are generally considered temporary, although their effect can be permanent depending on the process conditions, ease of regeneration, etc. Pgm catalyst(s) react readily with H₂S to form sulfides, which may or may not be stoichiometric. Sulfur may cause significant deactivation even at very low concentrations, due to the formation of strong metal-S bonds. Sulfur chemisorbs onto and reacts with the active catalyst sites, preventing reactant access. Furthermore, the stable metal-adsorbate bonds can lead to non-selective side reactions, which modify the surface chemistry.

Two reaction pathways are possible for S poisoning: bulk sulfidation and surface sulfidation, with the latter predominating. Initial surface sulfidation creates a diffusion barrier that hinders bulk sulfidation. Thus the pgm surface area per unit mass of catalyst must be optimised for maximum poison resistance. The temporary effect of S poisoning is used to advantage in the start-up of high-activity precious metal catalysts, such as platinum-based catalytic reforming catalysts. Fresh catalyst has too high an activity, and start-up conditions at feed-in may lead to thermal runaway, undesirable hydrocracking and dehydrogenation reactions. The above reactions can result in excessive carbon deposition, reduced yield and loss of cycle life. Low levels of S, introduced to the catalyst during manufacture or at start-up, are used to attenuate the initial high activity and allow the feed-in to be controlled without excessive coke laydown. Under normal operating conditions, with S-free feed, S adsorbed on the catalyst surface bleeds off, giving stable activity. From practical experience under normal operation, to prolong pgm catalyst life the concentrations of added H₂S (and other S species) should ideally be < 10 ppb.

The effects of poisons cannot be completely avoided, but can be reduced by a purification system designed to protect the pgm catalyst. Sub-optimal purification may lead to unnecessary costs associated with a loss of process economics and catalyst (regeneration or replacement). But, these can be insignificant compared to unscheduled production loss at a major catalytic unit.

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Reference


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